# Electronic Supplementary Information (ESI)

# Novel *ortho*-OPE Metallofoldamers: Binding-Induced Folding Promoted by Nucleating Ag(I)-Alkyne Interactions

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# SYNTHESIS AND CHARACTERIZATION

## General details

The following palladium catalysts, *trans*-dichlorobis(triphenylphosphine)palladium(II) ($Pd(PPh_3)_2Cl_2$) and *trans*-dichlorobis(acetonitrile)palladium(II) ($Pd(CH_3CN)_2Cl_2$), were prepared from palladium(II) chloride **(**$PdCl_2$) according to previously described procedures. [1] Palladium(II) chloride **(**$PdCl_2$), copper(I) iodide (CuI), trimethylsilyl acetylene (TMSA), triethylamine ($Et_3N$), *N,N*-diisopropylamine ($^iPr_2NH$), tri-tert-butylphosphonium tetrafluoroborate ($P^tBu_3{\cdot}HBF_4$), silver tetrafluoroborate ($AgBF_4$) and all other reagents were used as purchased from standard chemical suppliers and used without further purification. TLC was performed on aluminium-backed plates coated with silica gel 60 (230-240 mesh) with $F_{254}$ indicator. The spots were visualized with UV light (254 nm). All column chromatography were performed with silica gel 60 (35-70 μm) from VWR. The following known compounds were isolated as a pure samples and showed identical NMR spectra to the reported compound: **I, II,**[2] **III**, [2] **IV**, [3] **V**,[4] **1**, [5] **2**,[5] **3**,[5] **4**,[5] **5**,[5] **7**,[5] **8**,[6] **9**,[6] **10**[6] and **11**.[6]

NMR Spectra were measured at room temperature. $^1$H NMR spectra were recorded at 300, 400 or 500 MHz. Chemical shifts are reported in ppm using residual solvent peak as reference. Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, quint: quintuplet; m: multiplet, dd: doublet of doublets, dt: doublet of triplets, dq: doublet of quartets, td: triplet of doublets, bs: broad singlet), coupling constant (*J* in Hz) and integration. $^{13}$C NMR spectra were recorded at 75, 100 or 126 MHz using broadband proton decoupling and chemical shifts are reported in ppm using residual solvent peaks as reference. Carbon multiplicities were assigned by DEPT techniques.

High resolution mass spectra (HRMS) were recorded on a mass spectrometer using EI at 70eV, ESI and MALDI-TOF.

Absorption spectra were recorded at 25 °C with a Perkin-Elmer Lambda 650 UV/vis spectrophotometer equipped with a Peltier temperature-controlled cell holder. Steady-state fluorescence emission spectra were collected on a JASCO FP-6500 spectrofluorometer equipped with a 450 W xenon lamp for excitation, with temperature controller ETC-273T at 25 °C. All experiments were performed using 5×10-mm quartz cuvettes. Fluorescence decay traces were recorded in the single photon timing (SPT) mode using a FluoTime 200 fluorometer (PicoQuant, GmbH).

Single crystal X-ray diffraction data were recorded on a Bruker Kappa APEX II DUO diffractometer equipped with an APPEX 2 4K CCD area detector, a Microsource with Moka radiation and an Oxford Cryostream 700 low temperature device (T = -173ºC). Full-sphere data collection was used with w and j scans. Programs used: Data collection Apex2 V2009 1.0 (Bruker-Nonius 2008), data reduction Saint + Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008-1 (2008). Structure solution and refinement were carried out using SIR2011 and SHELXTL V6.14, respectively. All-non hydrogen atoms were refined including anisotropic displacement parameters.

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## General synthetic procedures

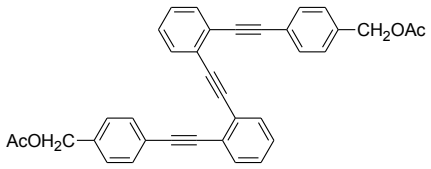
Sonogashira coupling of *aryl iodides*. ***(GP1)***

A solution of the terminal alkyne (1.2 mmol) dissolved in the minimum volume of THF and with 2 mL of $Et_3N$ was added dropwise to a carefully degassed solution of $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%) and the aryl iodide (1 mmol) in 10 mL of $Et_3N$. The reaction was stirred between 3-16 h at room temperature under argon atmosphere. The mixture was then diluted with EtOAc or dichloromethane, washed with saturated aq $NH_4Cl$ solution, dried over anhydrous $Na_2SO_4$ and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (EtOAc/Hexane mixtures) to give the corresponding coupling product.

*Sonogashira coupling of aryl bromides.* ***(GP2)***

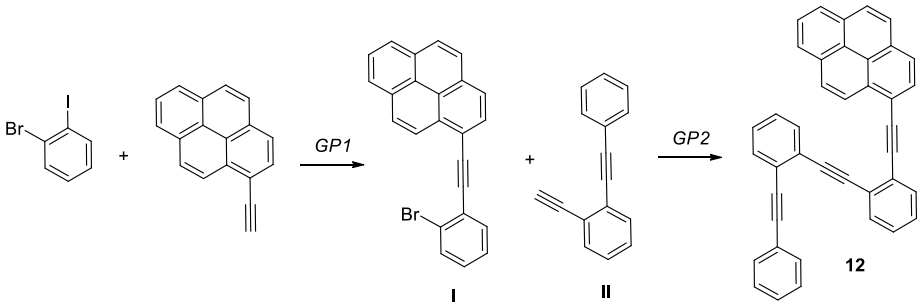
A solution of the terminal alkyne (1.2 mmol) dissolved in the minimum volume of THF and with 2 mL of $^{i}Pr_2NH$ was added dropwise to a carefully degassed solution of $Pd(CH_3CN)_2Cl_2$ (3 mol%), $P^{t}Bu_3{\cdot}HBF_4$ (6 mol%), CuI (3 mol%) and the aryl bromide (1 mmol) in 10 mL of $^{i}Pr_2NH$. The reaction was stirred between 3-16 h at room temperature under argon atmosphere. The mixture was then diluted with EtOAc or dichloromethane, washed with saturated aq $NH_4Cl$ solution, dried over anhydrous $Na_2SO_4$ and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (EtOAc/Hexane mixtures) to give the corresponding coupling product.

## Synthesis and characterization of the new *o*-OPEs 6 and 12-16




**6**

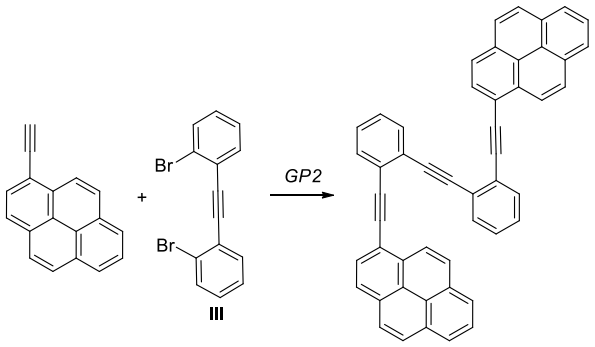
***Compounds* 6**. A drop of acetic anhydride was added to a solution of **4** (60 mg, 0.14 mmol) and DMAP (17 mg, 0.14 mmol) in dry $CH_2Cl_2$ ($10^{-3}$ M) and the reaction was stirring at room temperature for 1 hour. The solvent was then removed under reduced pressure and the residue was purified by flash chromatography (EtOAc/Hexane mixtures) to give **6** 49 % yield (36 mg) as white solid. $^1$H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 4H), 7.47 (d, *J* = 8.2 Hz, 4H), 7.37-7.33 (m, 4H), 7.25 (d, *J* = 8.2 Hz, 4H), 5.03 (s, 4H), 2.05 (s, 6H). $^{13}$C NMR (151 MHz, $CDCl_3$; DEPT) δ 171.0 (C), 137.2 (C), 132.6 (CH), 132.4 (CH), 132.2 (CH), 129.0 (CH), 128.8 (CH), 128.5 (CH), 126.1 (C), 126.0 (C), 123.3 (C), 93.8 (C), 92.6 (C), 88.9 (C), 66.1 ($CH_2$), 21.2 ($CH_3$). EI-HRMS calculated for $C_{36}H_{26}O_4$: 522.1831, found: 522.1834.




**I** **II** **12**

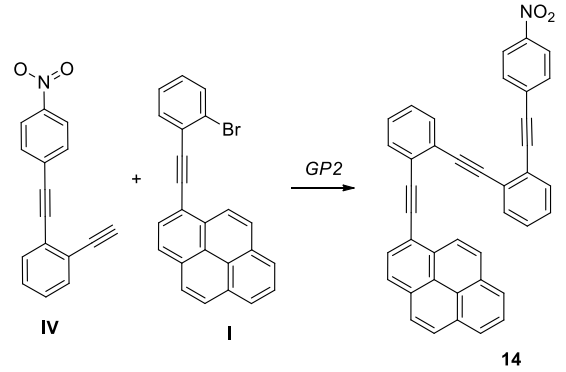
***Compound* I** was prepared from 1-bromo-2-iodobenzene (200 mg, 0.71 mmol) and 1-ethynyl-pyrene (160 mg, 0.7 mmol) according to previously described *GP1* to give **III** in 36 % yield (97 mg) as a bright yellow solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.84 (d, *J* = 9.1 Hz, 1H), 8.30-8.15 (m, 4H), 8.13-7.83 (m, 4H), 7.81–7.70 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 133.5 (CH), 132.7 (CH), 132.2 (C), 131.6 (C), 131.3 (C), 131.1 (C), 129.8 (CH), 129.5 (CH), 128.6 (CH), 128.4 (CH), 127.31 (CH), 127.29 (CH), 126.3 (CH), 125.9 (C), 125.8 (CHx2), 125.7 (CH), 125.7 (C), 124.6 (CH), 124.5 (C), 124.3 (C), 117.4 (C), 93.7 (C), 93.5 (C). EI-HRMS calculated for $C_{24}H_{13}Br$: 380.0200, found: 380.0201.

***Compound 12*** was prepared from intermediate **I** (200 mg, 0.71 mmol) and 1-ethynyl-2-(phenylethynyl)benzene **II** (160 mg, 0.7 mmol) according to previously described *GP2* to give **12** in 82 % yield brsm (39 mg) as a bright yellow solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 9.0 Hz, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 8.11 (d, *J* = 7.5 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 8.04 – 7.97 (m, 2H), 7.81 – 7.75 (m, 2H), 7.72 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.63 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.45 – 7.34 (m, 3H), 7.29 (td, *J* = 7.7, 1.4 Hz, 1H), 7.23 – 7.19 (m, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 132.6 (CH), 132.5 (CH), 132.2 (CH), 132.0 (CH), 131.8 (CHx2), 131.4 (C), 131.3 (C), 131.2 (C), 129.9 (CH), 128.5 (CH), 128.42 (CH), 128.40 (CH), 128.36 (CH), 128.1 (CH), 128.0 (CH), 127.3 (CH), 126.4 (C), 126.22 (CH), 126.20 (C), 126.1 (CH), 125.9 (C), 125.8 (C), 125.7 (CH), 125.6 (CH), 124.5 (CH), 124.5 (C), 124.3 (C), 123.3 (C), 117.9 (C), 94.1 (Cx2), 93.2 (C), 92.9 (C), 92.6 (C), 88.5 (C).

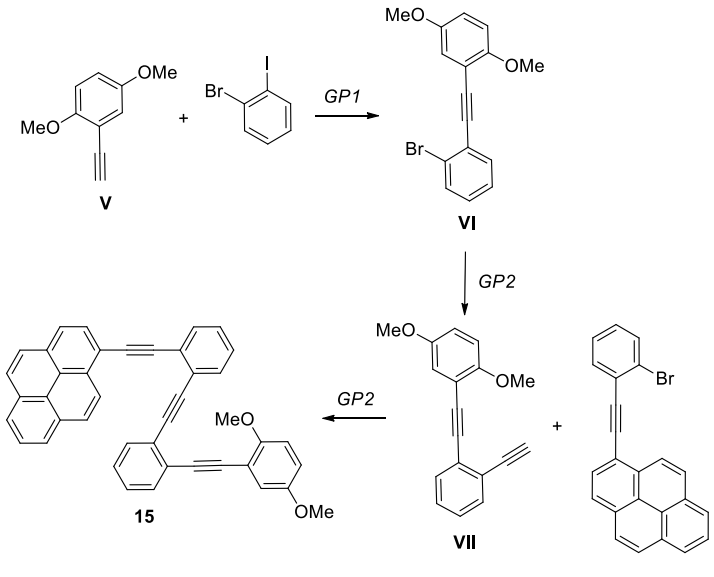



**III** **13**

***Compound* 13** was prepared from **III** (30 mg, 0.08 mmol) and 1-ethynyl-pyrene (50 mg, 0.22 mmol) according to previously described *GP2* to give **13** in 53 % yield (27 mg) as a bright yellow solid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 9.0 Hz, 2H), 8.10 (d, *J* = 7.0 Hz, 2H), 8.03 (d, *J* = 7.1 Hz, 2H), 7.97 (d, *J* = 7.7 Hz, 2H), 7.96 (t, *J* = 7.2 Hz, 2H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.80–7.76 (m, 6H), 7.56 (d, *J* = 9.1 Hz, 2H), 7.47 (td, *J* = 7.6, 1.2 Hz, 2H), 7.38 (td, *J* = 7.6, 1.2 Hz, 2H),; $^{13}$C NMR (126 MHz, $CDCl_3$) δ 132.9 (CH), 132.2 (CH), 131.9 (C), 131.2 (Cx2), 131.1 (C), 131.0 (C), 129.8 (CH), 129.0 (C), 128.5 (CH), 128.1 (CHx2), 128.0 (CH), 127.1 (CH), 126.7 (C), 126.1 (CH), 125.9 (CH), 125.8 (C), 125.6 (CH), 125.4 (CH), 124.2 (CH), 124.1 (C), 117.7 (C), 94.1 (C), 93.5 (C), 93.0 (C); MALDI-HRMS calculated for $C_{50}H_{26}$: 626.2048, found: 626.2029.

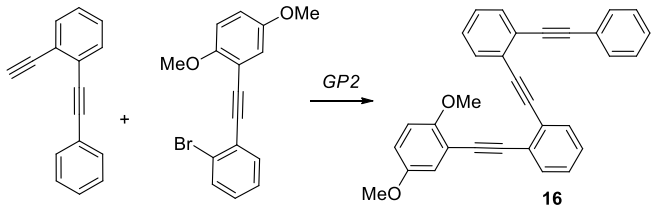



***Compound* 14** was prepared from **IV** (100 mg, 0.4 mmol) and **I** (111 mg, 0.29 mmol) according to previously described *GP2* to give **14** in 57 % yield (91 mg) as a pale yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 9.1 Hz, 1H), 8.19 (d, *J* = 7.4 Hz, 1H), 8.09 (dd, *J* = 8.0, 4.4 Hz, 3H), 8.04 – 7.97 (m, 3H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.76 – 7.67 (m, 5H), 7.61 – 7.55 (m, 1H), 7.51 – 7.36 (m, 4H), 7.24 (d, *J* = 8.4 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 146.4 (C), 132.8 (CH), 132.5 (CH), 132.5 (CH), 132.3 (CH), 132.3 (CH), 132.1 (C), 132.0 (CH), 131.4 (C), 131.2 (C), 131.1 (C), 130.0 (C), 129.8 (CH), 129.0 (C), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.3 (CH), 126.4 (CH), 126.2 (C), 126.1 (CH), 125.8 (C), 125.7 (CH), 125.5 (CH), 125.2 (C), 124.4 (CH), 124.3 (C), 124.2 (C), 123.7 (CH), 123.0 (CH), 117.7 (C), 94.0 (C), 93.5 (C), 93.3 (C), 93.2 (C), 92.1 (C), 92.0 (C). ESIpos-HRMS calculated for $C_{42}H_{26}O_2Na$ $[M+Na]^+$: 585.1847, found: 585.1825.




***Compound* VI** was prepared from **V** (263 mg, 1.62 mmol) and 1-bromo-2-iodobenzene (458 mg, 1.62 mmol) according to previously described *GP1* to give **VI** in 45 % yield (230 mg) as a transparent liquid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.60 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.28 (td, *J* = 7.6, 1.4 Hz, 1H), 7.17 (td, *J* = 7.8, 1.7 Hz, 1H), 7.09 (d, *J* = 3.1 Hz, 1H), 6.89 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 154.8 (C), 153.4 (C), 133.5 (CH), 132.5 (CH), 129.4 (CH), 127.1 (CH), 125.73 (C), 125.70 (C), 118.3 (CH), 116.3 (CH), 112.9 (C), 112.5 (CH), 92.0 (C), 90.5 (C), 56.8 (CH3), 55.6 (CH3); EI-HRMS calculated for $C_{16}H_{14}BrO_2$ $[M+H^+]$: 317.0165, found: 317.0177.

***Compound* 15. VII** was prepared from **VI** (260 mg, 0.82 mmol) and TMSA (0.2 mL, 1.23 mmol) according to previously described *GP2* in 45 % yield (230 mg) as a transparent liquid. This intermediate **VII** (23 mg, 0.09 mmol) was cross-coupled with **I** (32 mg, 0.0.9 mmol) according to previously described *GP2* to give **16** in 51 % yield (25 mg) as a pale yellow solid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 9.0 Hz, 1H), 8.20 – 8.17 (m, 2H), 8.12 – 8.06 (m, 3H), 8.02 (d, *J* = 8.9 Hz, 1H), 7.99 (t, *J* = 7.6 Hz, 1H), 7.76 – 7.73 (m, 3H), 7.68 (d, *J* = 7.8, 2H),), 7.43-7.38 (m, 2H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 (td, *J* = 7.6, 1.3 Hz,1H), 6.95 (d, *J* = 3.0 Hz, 1H), 6.70 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.65 (d, *J* = 9.0 Hz, 1H), 3.65 (s, 3H), 3.55 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 154.5 (C), 153.1 (C), 132.7 (CH), 132.5 (CH), 132.2 (C), 132.1 (CH), 132.0 (CH), 131.4 (C), 131.3 (C), 131.2 (C), 129.9 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.0 (CH), 127.9 (CH), 127.4 (CH), 126.7 (C), 126.2 (CH), 126.2 (C), 126.2 (CH), 125.93 (C), 125.90 (C), 125.7 (CH), 125.5 (CH), 124.53 (CH), 124.51 (C), 124.4 (C), 117.9 (C), 117.7 (CH), 116.6 (CH), 112.9 (C), 112.1 (CH), 94.1 (C), 93.3 (C), 92.7 (C), 92.7 (C), 92.4 (C), 90.7 (C), 56.4 (CH3), 55.6 (CH3); ESIpos-HRMS calculated for $C_{42}H_{26}O_2Na$ [M+Na$^+$]: 585.1847, found: 585.1825.




***Compound* 16** was prepared from **VI** (60 mg, 0.19 mmol) and 1-ethynyl-2-(phenylethynyl)benzene **II** (50 mg, 0.25 mmol) according to previously described *GP2* to give **16** in 33 % yield (27 mg) as a transparent liquid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.60 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.53-7.50 (m, 2H), 7.35 – 7.27 (m, 7H), 7.05 (d, *J* = 3.0 Hz, 1H), 6.82 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 1H), 3.76 (s, 3H), 3.66 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 154.7 (C), 153.3 (C), 132.4 (CH), 132.1 (CH), 132.0 (CH), 131.8 (CHx2), 131.8 (CH), 128.4 (CH), 128.4 (CHx2), 128.24 (CH), 128.22 (CH), 128.00 (CH), 127.98 (CH), 126.2 (C), 126.1 (C), 125.93 (C), 125.90 (C), 123.3 (C), 117.9 (CH), 116.7 (CH), 113.0 (C), 112.3 (CH), 93.9 (C), 92.6 (C), 92.3 (C), 92.3 (C), 90.4 (C), 88.4 (C), 56.6 ($CH_3$), 55.8 ($CH_3$); ESIpos-HRMS calculated for $C_{32}H_{22}O_2Na$ [M+Na$^+$]: 461.1518, found: 461.1512.

## Spectroscopical characterization of the Ag(I)-complexes

**Complex 1·Ag(I):** $^{1}$H NMR (500 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.93–7.91 (m, 2H), 7.87–7.85 (m, 2H), 7.63–7.57 (m, 4H), 7.45 (d, *J* = 8.4 Hz, 4H), 7.22 (d, *J* = 8.4 Hz, 4H), 5.18 (s, 4H), 3.57 (s, 2H); $^{13}$C NMR (126 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 166.4 (C), 139.3 (C), 135.0 (CH), 134.0 (CH), 133.2 (CH), 131.2 (CH), 131.1 (CH), 129.0 (CH), 124.9 (C), 122.6 (C), 118.6 (C), 96.4 (C), 93.1 (C), 85.8 (C), 66.6 ($CH_2$), 42.5 ($CH_2$).

**Complex 2·Ag(I):** $^{1}$H NMR (600 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 7.85 (d, *J* = 8.9 Hz, 2H), 7.64 – 7.56 (m, 4H), 7.44 (d, *J* = 8.2 Hz, 4H), 7.20 (d, *J* = 8.2 Hz, 4H), 5.15 (s, 4H), 2.81 (s, 4H). $^{13}$C NMR (126 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 172.3 (C), 140.0 (C), 134.7 (CH), 133.9 (CH), 133.1 (CH), 131.2 (CH), 131.0 (CH), 128.2 (CH), 124.9 (C), 122.9 (C), 118.5 (C), 96.2 (C), 92.9 (C), 85.7 (C), 65.8 ($CH_2$), 30.0 ($CH_2$).

**Complex 3·Ag(I):** $^{1}$H NMR (400 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.81 (dd, *J* = 6.7, 2.4 Hz, 2H), 7.72 (dd, *J* = 6.6, 2.3 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.45-7.40 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 4H), 7.05 (d, *J* = 8.2 Hz, 4H), 5.29 (s, 2H), 5.23 (d, *J* = 13.4 Hz, 2H), 4.91 (d, *J* = 13.4 Hz, 2H), 1.15 (s, 18H). A good quality $^{13}$C NMR spectrum could not be obtained even using long acquisition period owing to the concentration used. Higher concentrations resulted in precipitation of the sample.

**Complex 4·Ag(I):** $^{1}$H NMR (400 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.78 – 7.75 (m, 2H), 7.70 – 7.67 (m, 2H), 7.47 – 7.44 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.16 (s, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.27 (q, *J* = 8.1 Hz, 2H), 5.04 (s, 2H), 4.91 (d, *J* = 13.4 Hz, 1H), 4.74 (d, *J* = 13.5 Hz, 1H), 1.17 (s, 9H), 1.15 (s, 9H). A good quality $^{13}$C NMR spectrum could not be obtained even using long acquisition period owing to the concentration used. Higher concentrations resulted in precipitation of the sample.

**Complex 5·Ag(I):** $^{1}$H NMR (400 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.75 – 7.71 (m, 2H), 7.67 – 7.63 (m, 2H), 7.46 – 7.41 (m, 4H), 7.40 (d, *J* = 5.3 Hz, 2H), 7.23 (s, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 2H), 5.24 (s, 2H), 4.95 (d, *J* = 13.0 Hz, 2H), 4.80 (d, *J* = 13.0 Hz, 2H), 1.13 (s, 18H). A good quality $^{13}$C NMR spectrum could not be obtained even using long acquisition period owing to the concentration used. Higher concentrations resulted in precipitation of the sample.

**Complex 6·Ag(I):** $^{1}$H NMR (500 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.88 (dd, *J* = 6.1, 3.0 Hz, 2H), 7.80 (dd, *J* = 6.0, 3.1 Hz, 2H), 7.57-7.53 (m, 4H), 7.44 (d, *J* = 8.1 Hz, 4H), 7.20 (d, *J* = 8.1 Hz, 4H), 5.07 (s, 4H), 2.12 (s, 6H); $^{13}$C NMR (126 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 172.0 (C), 139.5 (C), 134.3 (CH), 133.7 (CH), 132.8 (CHx2), 131.0 (CH), 130.6 (CH), 128.2 (CHx2), 125.0 (C), 123.1 (C), 118.8 (C), 95.4 (C), 92.5 (C), 85.5 (C), 65.8 ($CH_2$), 21.1 ($CH_3$).

**Complex 7·Ag(I):** $^{1}$H NMR (400 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.89 (bd, *J* = 9.2 Hz, 2H), 7.83 (bd, *J* = 8.8 Hz, 2H), 7.63 – 7.53 (m, 4H), 7.42 (d, *J* = 8.0 Hz, 4H), 7.21 (d, *J* = 8.1 Hz, 4H), 4.68 (s, 4H); $^{13}$C NMR (126 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 144.7 (C), 134.2 (CH), 133.7 (CH), 132.7 (CH), 130.8 (CH), 130.5 (CH), 127.3 (CH), 125.2 (C), 123.3 (C), 118.4 (C), 95.7 (C), 92.6 (C), 85.4 (C), 64.8 ($CH_2$).

**Complex 8·Ag(I):** $^{1}$H NMR (500 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.87 (dd, *J* = 6.0, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.59 – 7.54 (m, 4H), 7.46 – 7.41 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 4H). $^{13}$C NMR (126 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 134.4 (CH), 133.8 (CH), 132.7 (CHx2), 131.1 (CH), 131.0 (CH), 130.7 (CH), 129.3 (CHx2), 125.1 (C), 123.1 (C), 119.2 (C), 96.0 (C), 92.6 (C), 85.3 (C).

**Complex 9·Ag(I):** $^{1}$H NMR (500 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.94 – 7.88 (m, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.63 – 7.59 (m, 2H), 7.47 – 7.38 (m, 8H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 4H),); $^{13}$C NMR (126 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 134.6 (CH), 133.6 (CH), 133.5 (CH), 132.7 (CHx2), 131.4 (CH), 131.3 (CH), 130.9 (CH), 130.4 (CH), 129.2 (CHx2), 125.3 (C), 123.9 (C), 122.4 (C), 120.2 (C), 97.4 (C), 93.6 (C), 91.8 (C), 87.0 (C).

**Complex 10·Ag(I):** $^{1}$H NMR (500 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.73 (bd, *J* = 7.5 Hz, 2H), 7.71 – 7.67 (m, 2H), 7.48 – 7.38 (m, 12H), 7.30 (td, *J* = 7.7, 1.0 Hz, 2H), 7.11 – 7.01 (m, 8H); $^{13}$C NMR (126 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 134.3 (CH), 134.0 (CH), 132.8 (CH), 132.5 (CHx2), 132.4 (CH), 131.10 (CH), 131.09 (CH), 130.8 (CH), 130.7 (CH), 130.1 (CH), 129.0 (CHx2), 125.1 (C), 123.6 (C), 122.9 (C), 122.4 (C), 120.5 (C), 97.6 (C), 94.3 (C), 92.5 (C), 92.0 (C), 87.7 (C).

**Complex 11·Ag(I):** $^{1}$H NMR (600 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.31-7.27 (m, 6H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.21-7.18 (m, 4H), 7.10 (d, *J*

= 7.7 Hz, 2H), 7.02 (t, *J* = 7.1 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 4H); $^{13}$C NMR (151 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 133.9 (CH), 133.7 (CH), 133.4 (CH), 133.1 (CH), 132.35 (CH), 132.30 (CH), 131.0 (CH), 130.9 (CH), 130.7 (CH), 130.4 (CH), 130.0 (CH), 129.4 (CH), 128.6 (CH), 125.7 (C), 123.9 (C), 122.9 (C), 122.8 (C), 122.7 (C), 121.3 (C), 97.6 (C), 95.3 (C), 92.9 (C), 92.8 (C), 92.1 (C), 88.1 (C).

**Complex 12·Ag(I):** $^{1}$H NMR (500 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 8.48 (d, *J* = 9.0 Hz, 1H), 8.34 (d, *J* = 7.6 Hz, 1H), 8.29 (d, *J* = 7.5 Hz, 1H), 8.25 (d, *J* = 8.9 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.13-8.08 (m, 3H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.95-7.90 (m, 3H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.62-7.54 (m, 4H), 6.84 (d, *J* = 7.3 Hz, 2H), 6.43 (t, *J* = 7.6 Hz, 1H), 6.27 (t, *J* = 7.8 Hz, 2H); $^{13}$C NMR (126 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 134.6 (CH), 134.5 (CH), 134.0 (CH), 133.8 (CH), 133.6 (C), 132.7 (C), 131.6 (CHx2), 131.5 (C), 131.15 (CH), 131.11 (C), 131.0 (CH), 130.8 (CH), 130.7 (CH), 130.1 (CH), 129.9 (CHx2), 128.1 (CHx2), 127.3 (CH), 127.2 (CH), 127.11 (CH), 127.10 (CH), 125.7 (C), 125.3 (CH), 125.2 (C), 124.7 (C), 124.3 (C), 124.2 (CH), 123.41 (C), 123.37 (C), 118.0 (C), 112.4 (C), 95.5 (C), 95.0 (C), 93.3 (C), 92.8 (C), 90.0(C), 84.6 (C).

**Complex 13·Ag(I):** $^{1}$H NMR (500 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 8.11 (d, *J* = 9.0 Hz, 2H), 8.01 (bd, *J* = 9.0 Hz, 2H), 7.92 (bd, *J* = 7.5 Hz, 2H), 7.89 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.76 (t, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 9.0 Hz, 2H), 7.65 (td, *J* = 7.7, 1.5 Hz, 2H), 7.62 (td, *J* = 7.5, 1.5 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H); $^{13}$C NMR (126 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 134.7 (CH), 134.0 (CH), 132.8 (C), 132.0 (C), 131.1 (CH), 130.9 (CH), 130.8 (C), 130.4 (C), 129.9 (CH), 129.7 (CH), 129.5 (CH), 126.9 (CH), 126.70 (CH), 126.68 (CH), 126.6 (CH), 125.9 (CH), 124.4 (CH), 123.8 (C), 123.6 (CH), 123.5 (C), 123.1 (C), 111.4 (C), 95.1 (C), 93.5 (C), 89.5 (C).

**Complex 14·Ag(I):** $^{1}$H NMR (400 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 8.56 (d, *J* = 9.0 Hz, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 8.24 (d, *J* = 7.7 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.9 Hz, 1H), 8.10 (t, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 6.4 Hz, 1H), 8.00 (d, *J* = 6.4 Hz, 1H), 7.92 - 7.86 (m, 3H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.62 – 7.50 (m, 4H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR (151 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 147.0 (C), 133.4 (CH), 133.2 (CH), 132.9 (CH), 132.6 (C), 132.5 (CH), 132.41 (C), 132.39 (C), 131.5 (C), 131.2 (C), 130.6 (CH), 130.3 (CH), 130.1 (CH), 130.0 (CH), 129.7 (CH), 129.00 (CH), 128.97 (CH), 128.1 (C), 127.1 (CH), 126.7 (CH), 126.53 (CH), 126.50 (CH), 125.9 (C), 125.1 (CH), 125.0 (CH), 124.9 (C), 124.7 (C), 124.5 (C), 124.3 (C), 124.0 (CH), 123.2 (CH), 116.0 (C), 93.9 (C), 93.1 (C), 92.8 (C), 92.6 (C), 92.3 (C), 91.9 (C).

**Complex 15·Ag(I):** $^{1}$H NMR (600 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 8.56 (d, *J* = 9.0 Hz, 1H), 8.34 (d, *J* = 7.5 Hz, 1H), 8.29 (d, *J* = 7.5 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 8.15 - 8-13 (m, 2H), 8.04 (d, *J* = 8.9 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.96-7.92 (m, 3H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.55 (m, 4H), 6.16 (s, 1H), 5.81 (dd, *J* = 9.0, 2.7 Hz, 1H), 5.57 (d, *J* = 9.1 Hz, 1H), 3.35 (s, 3H), 3.13 (s, 3H); $^{13}$C NMR (151 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 152.9 (C), 151.3 (C), 134.5 (CH), 134.11 (CH), 134.10 (CH), 133.6 (CH), 133.6 (C), 132.5 (C), 131.5 (C), 131.2 (CH), 131.0 (CH), 130.9 (CH), 130.8 (CH), 130.6 (CH), 130.1 (CH), 129.8 (CH), 127.2 (CH), 127.2 (CH), 127.0 (CH), 126.9 (C), 125.5 (C), 125.1 (CH), 124.5 (C), 124.4 (C), 124.2 (C), 124.1 (CH), 123.3 (C), 122.8 (C), 117.4 (CH), 117.1 (CH), 112.5 (C), 110.8 (CH), 106.8 (C), 95.2 (C), 93.7 (C), 93.2 (C), 90.4 (C), 90.3 (C), 90.2 (C), 57.2 ($CH_3$), 55.4 ($CH_3$).

**Complex 16·Ag(I):** $^{1}$H NMR (500 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.88-7.83 (m, 4H), 7.59 – 7.55 (m, 4H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 3.1 Hz, 1H), 6.90 (dd, *J* = 9.2, 3.1 Hz, 1H), 6.53 (d, *J* = 9.2 Hz, 1H), 3.77 (s, 3H), 3.58 (s, 3H); $^{13}$C NMR (126 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 154.3 (C), 152.9 (C), 134.5 (CH), 134.2 (CH), 134.0 (CH), 133.7 (CH), 132.7 (CHx2), 131.21 (CH), 131.18 (CH), 131.1 (CH), 130.9 (CH), 130.8 (CH), 129.3 (CHx2), 125.2 (C), 124.7 (C), 123.1 (C), 122.9 (C), 119.3 (CH), 118.7 (CH), 112.6 (CH), 96.5 (C), 93.3 (C), 92.9 (C), 91.0 (C), 90.8 (C), 85.5 (C), 57.2 ($CH_3$), 56.4 ($CH_3$), (two carbon signals were not observed).

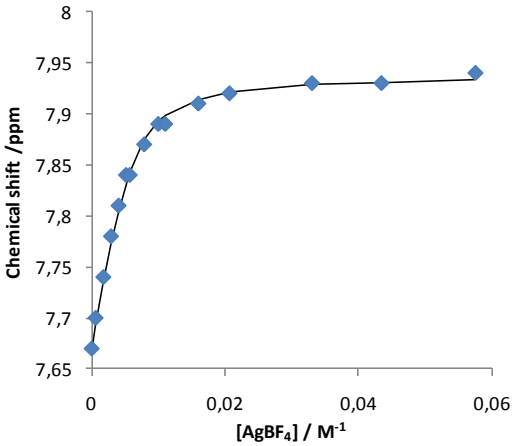
## $^{1}$H-NMR titrations and binding constant determination

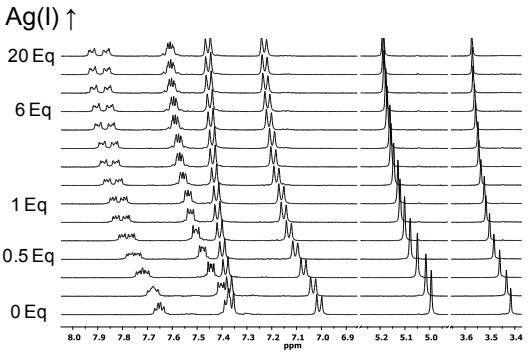
A stock solution of the ligands ($10^{-2}$-$10^{-3}$M) in $CD_2Cl_2$/Acetone-*d*6 (v/v, 9:1) was firstly prepared. Using this solution as a solvent, a stock solution of $AgBF_4$ (20-200 mM depending on the ligand) was prepared. Then, 0.5 mL of the pure ligand solution was transferred to a NMR tube and initial spectra was registered. To this solution, small portions of the silver solution were added and the spectra recorded after each addition. Binding constants were determined by non-linear regression curve fitting methods using Program DynaFit[7] plotting the differences measured between the initial chemical shifts of the selected protons[8] against the concentration of the silver added.

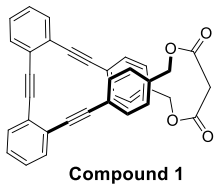
| Compound | Ka ($M^{-1}$) ± SD |
|---|---|
| **1** | 1001±180 |
| **2** | 852±260 |
| **3** | 48.6±2.2 |
| **4** | 739±140 |
| **5** | 63.1±5.5 |
| **6** | 86.2±7.4 |
| **7** | 53.4±1.6 |
| **8** | 318±25 |
| **9** | 667±50 |
| **10** | 680 ± 24 |
| **11** | 559 ± 16 |
| **12** | 71±17 |
| **13** | 22.2±4.7 |
| **14** | 7.30±0.25 |
| **15** | 187±84 |
| **16** | $>10^5$ $M^{-1}$ |

[7] P. Kuzmic, *Analytical Biochemistry*, **1996**, *237*, 260-273.

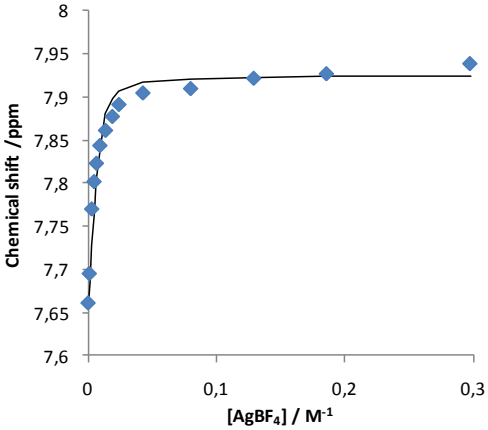
[8] For the calculations all the identifiable signals were included in a global fitting except for the indicated cases.

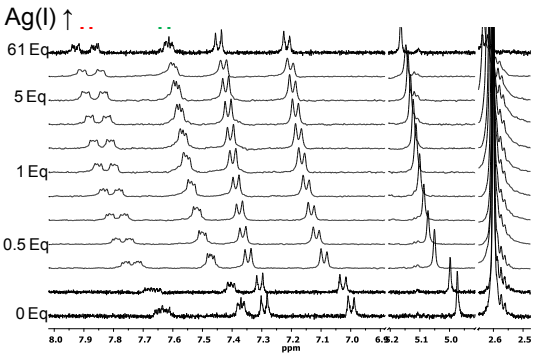


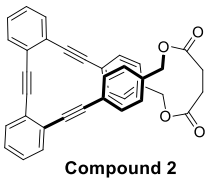



Compound 1



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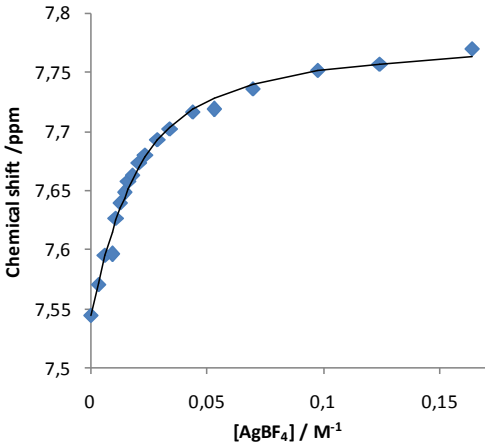


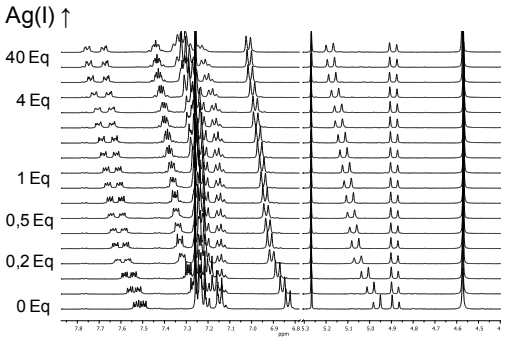


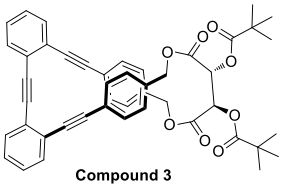

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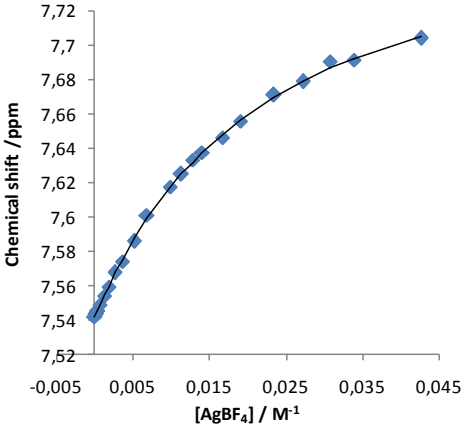


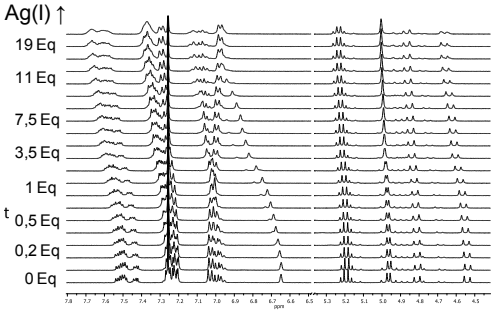


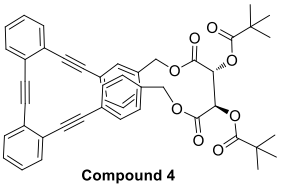

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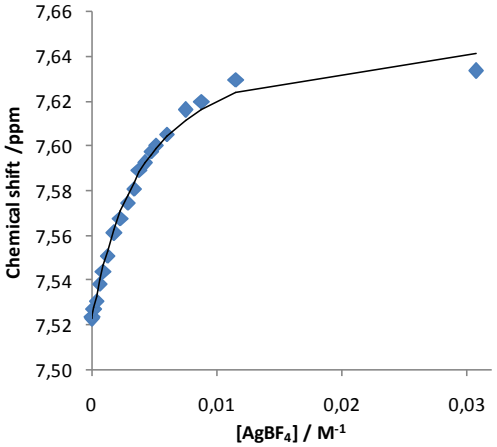


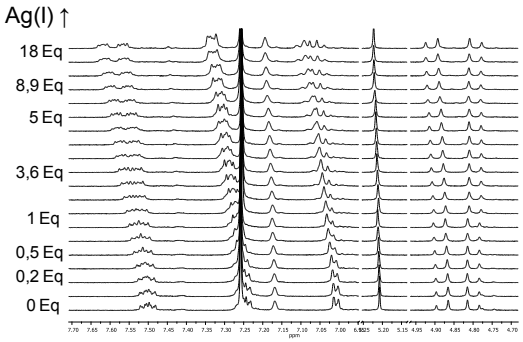


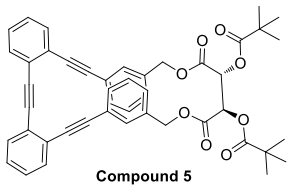

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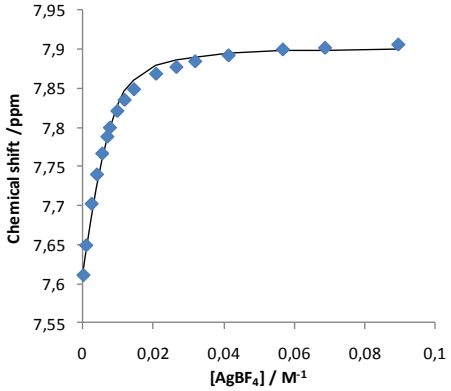


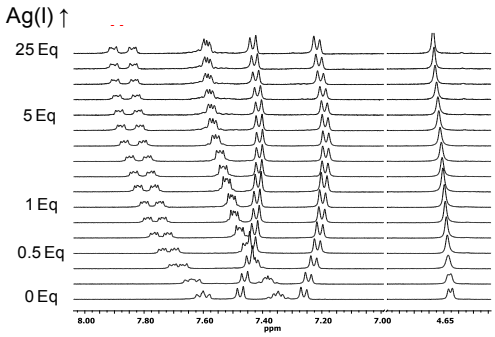


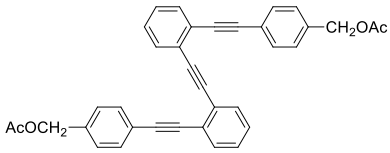


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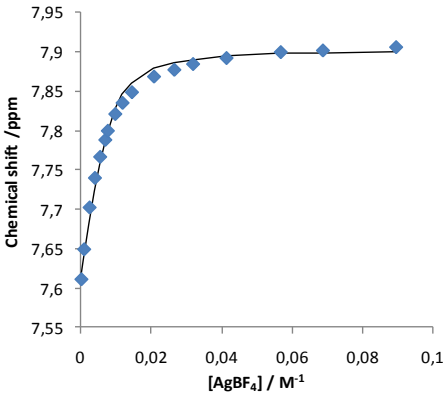
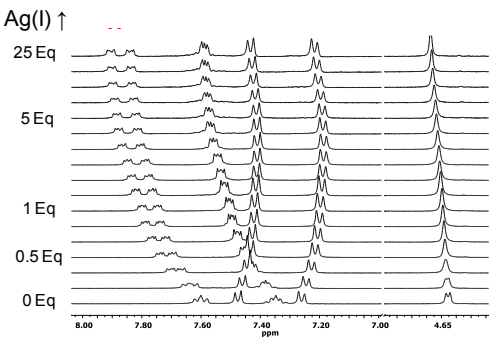
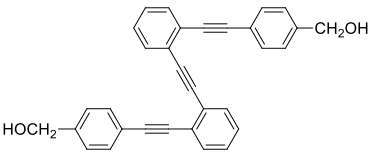
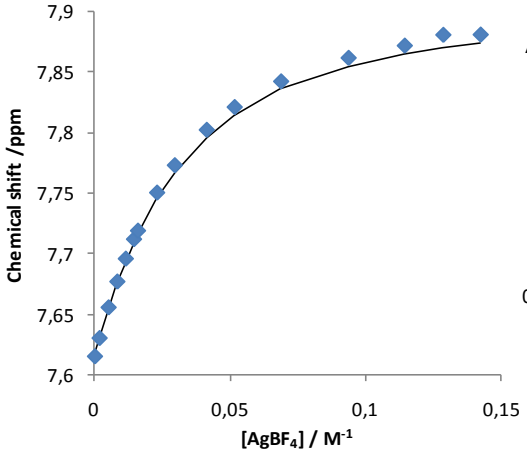
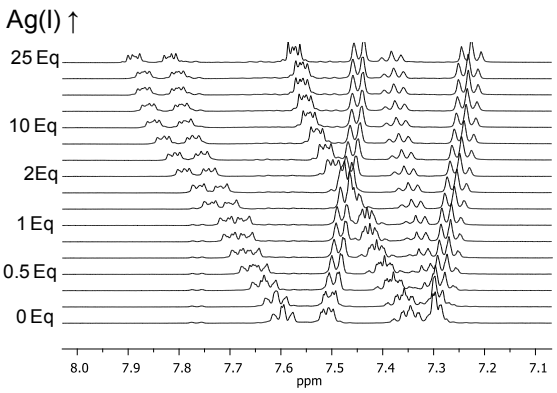


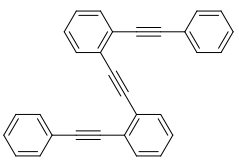



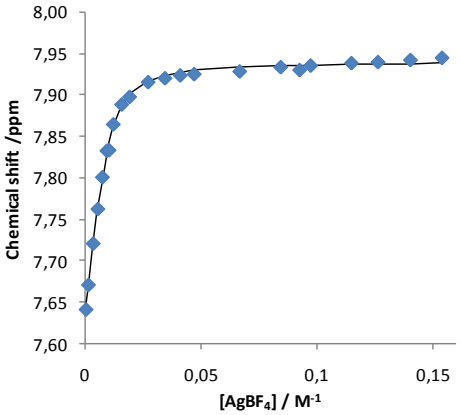

Compound 7

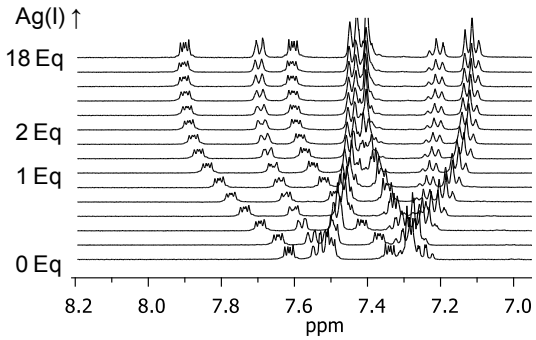


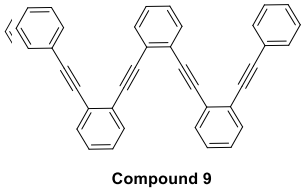



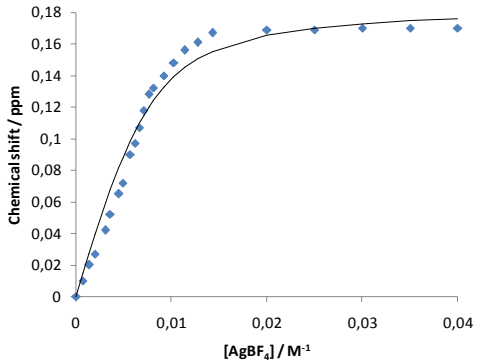
Compound 8

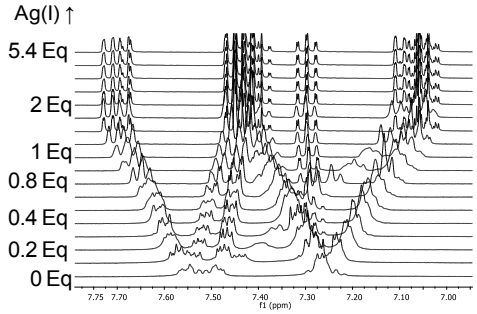


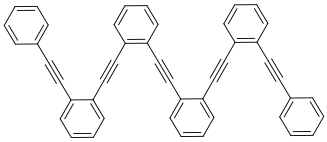



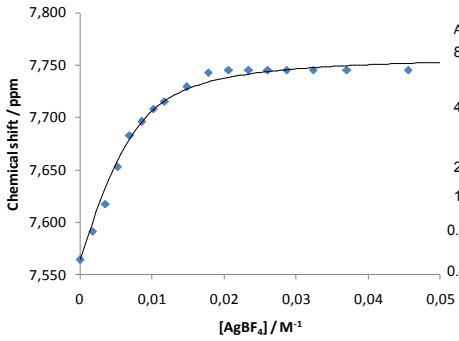
Compound 9

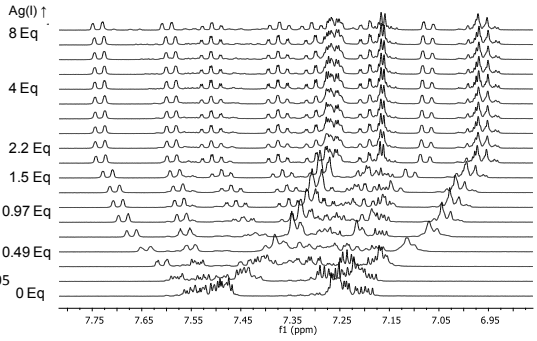


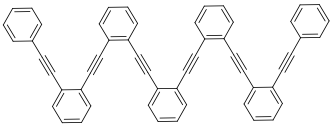



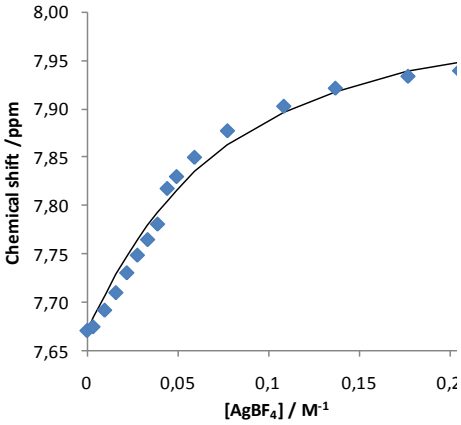
Compound 10

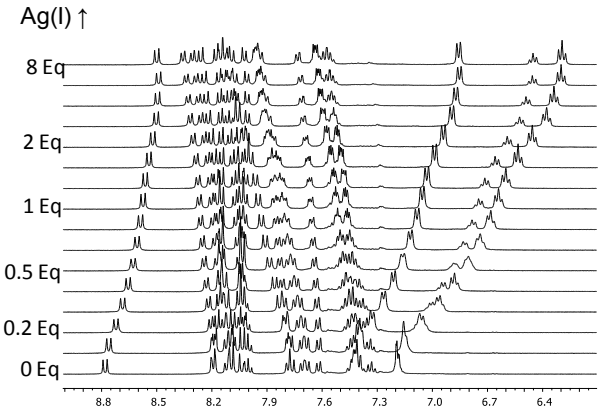


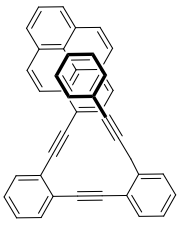



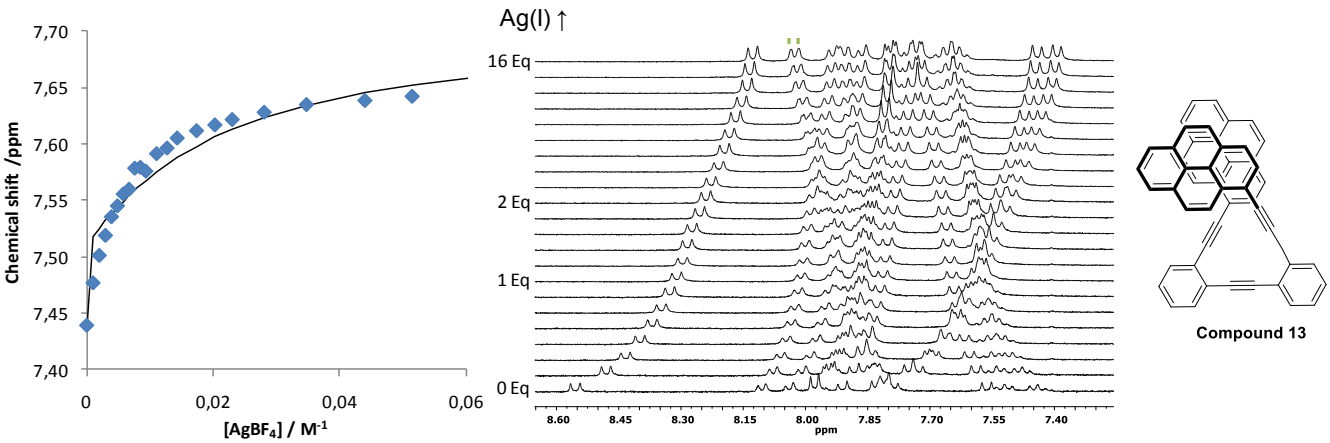
Compound 11

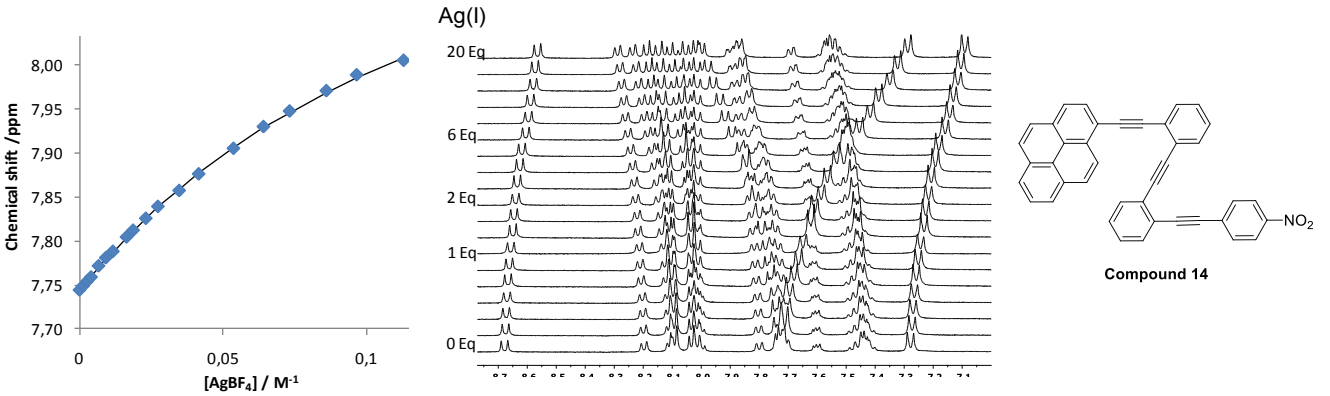


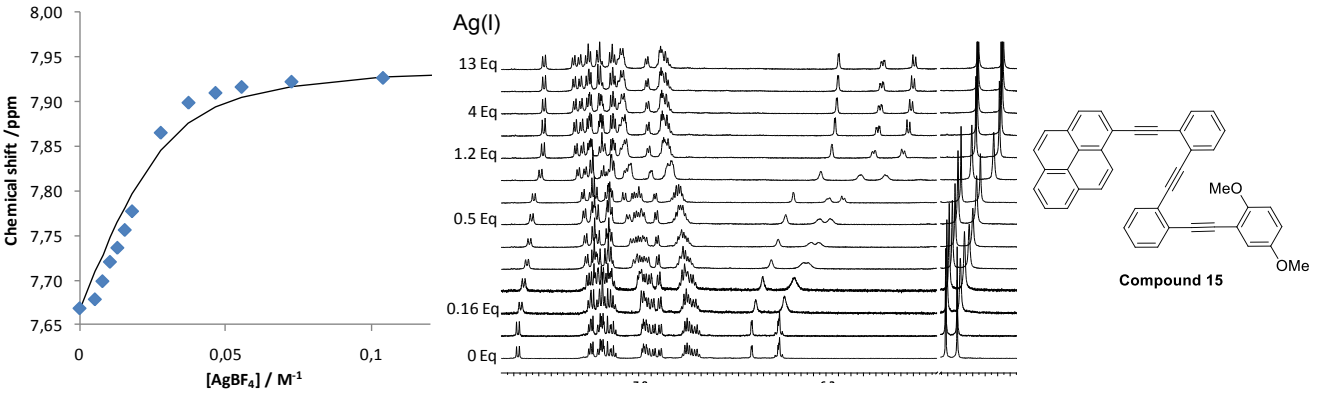



Compound 12


Ag(I) ↑
Chemical shift /ppm
[AgBF4] / M-1
16 Eq
2 Eq
1 Eq
0 Eq
ppm
Compound 13


Ag(I)
Chemical shift /ppm
[AgBF4] / M-1
20 Eq
6 Eq
2 Eq
1 Eq
0 Eq
NO2
Compound 14


Ag(I)
Chemical shift /ppm
[AgBF4] / M-1
13 Eq
4 Eq
1.2 Eq
0.5 Eq
0.16 Eq
0 Eq
MeO
OMe
Compound 15

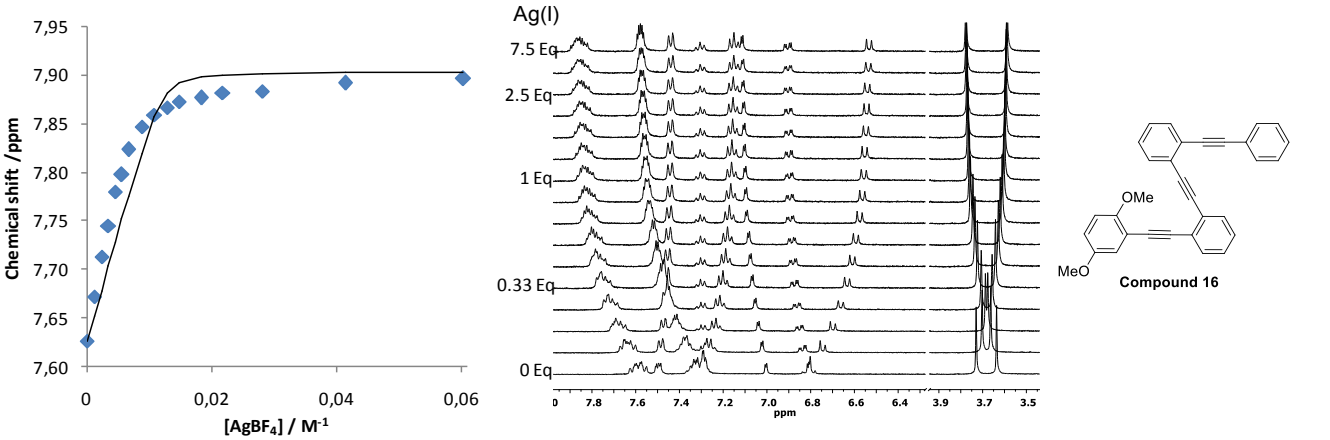

Ag(I)
Chemical shift /ppm
[AgBF4] / M-1
7.5 Eq
2.5 Eq
1 Eq
0.33 Eq
0 Eq
ppm
OMe
MeO
Compound 16

**Figure S1: Influence of silver coordination evaluated in the $^{1}H$ and $^{13}C$ NMR data of 1 and 6.**

In the work of Pale et al. (ref. 18 manuscript), three important aspects were used to evidence the in situ formation of a Ag(I)- alkyne complex:
1) a decrease on the coupling constant $^{4}J\{^{1}H,^{1}H\}$ of the neighboring protons which indicated a loss of electron density of the triple bond,
2) the deshielding of the alkyne neighboring protons and
3) the shielding of the internal sp carbon which was accompanied by a deshielding of the terminal carbon.
Interestingly, analogous hints of coordination were recorded in our case (See Figure S1).

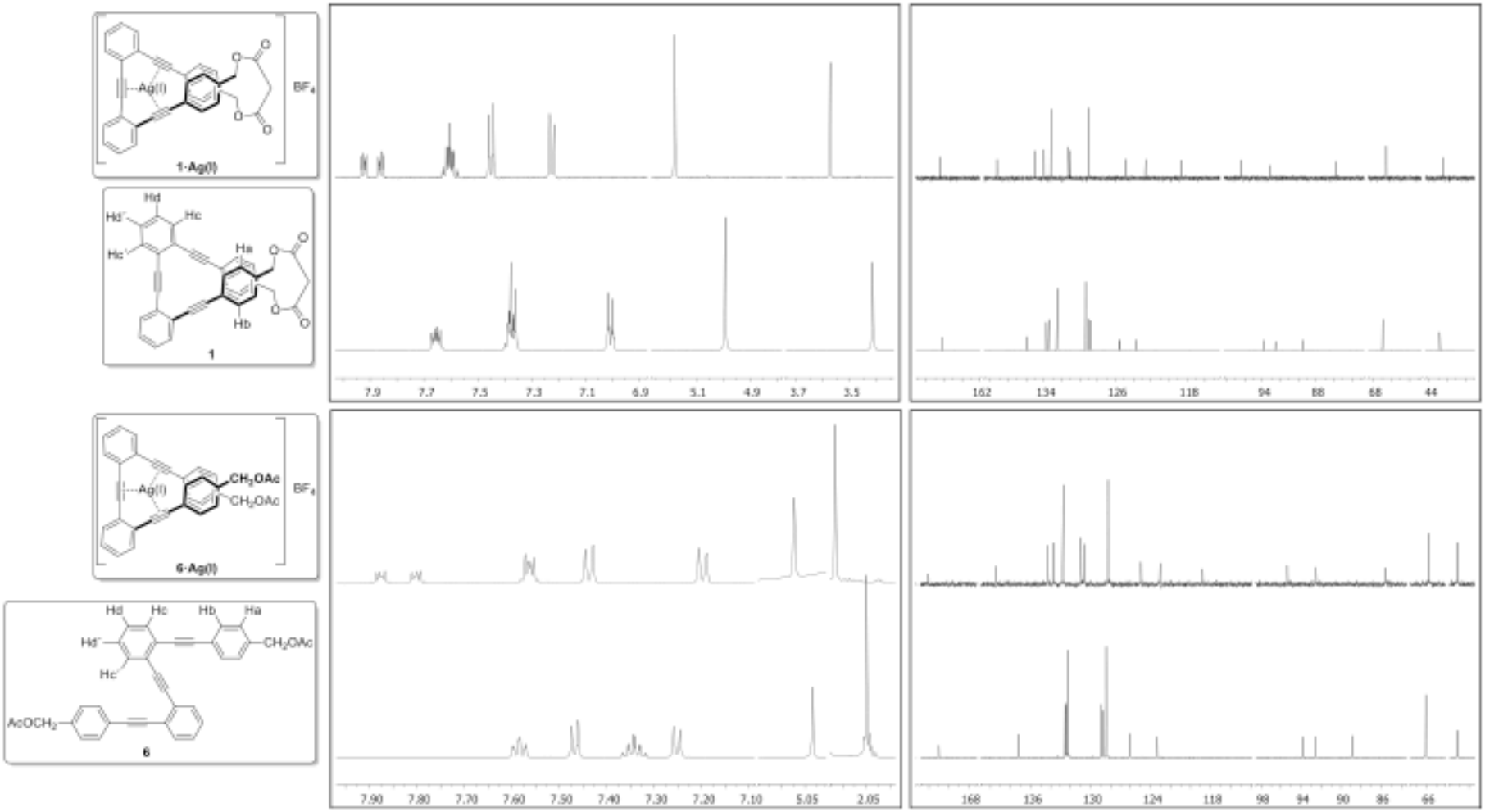


**Figure S2: $^{1}$H-NMR spectra and titration curves for tolane, 1,2-bis(phenylethynyl)benzene and 1,3-bis((2-(phenylethynyl)phenyl)ethynyl)benzene.**

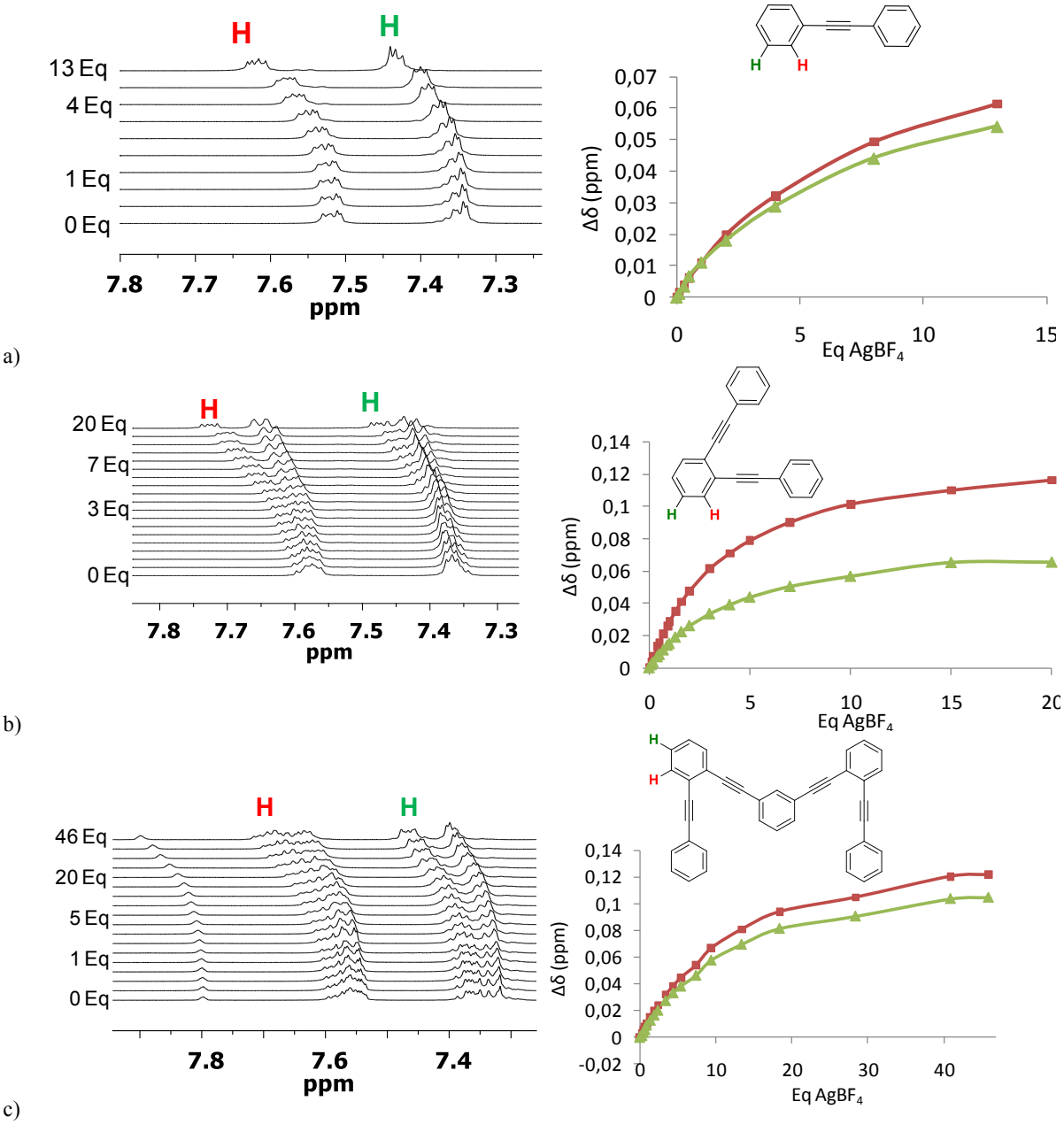
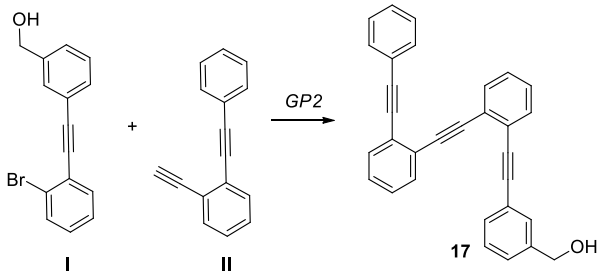


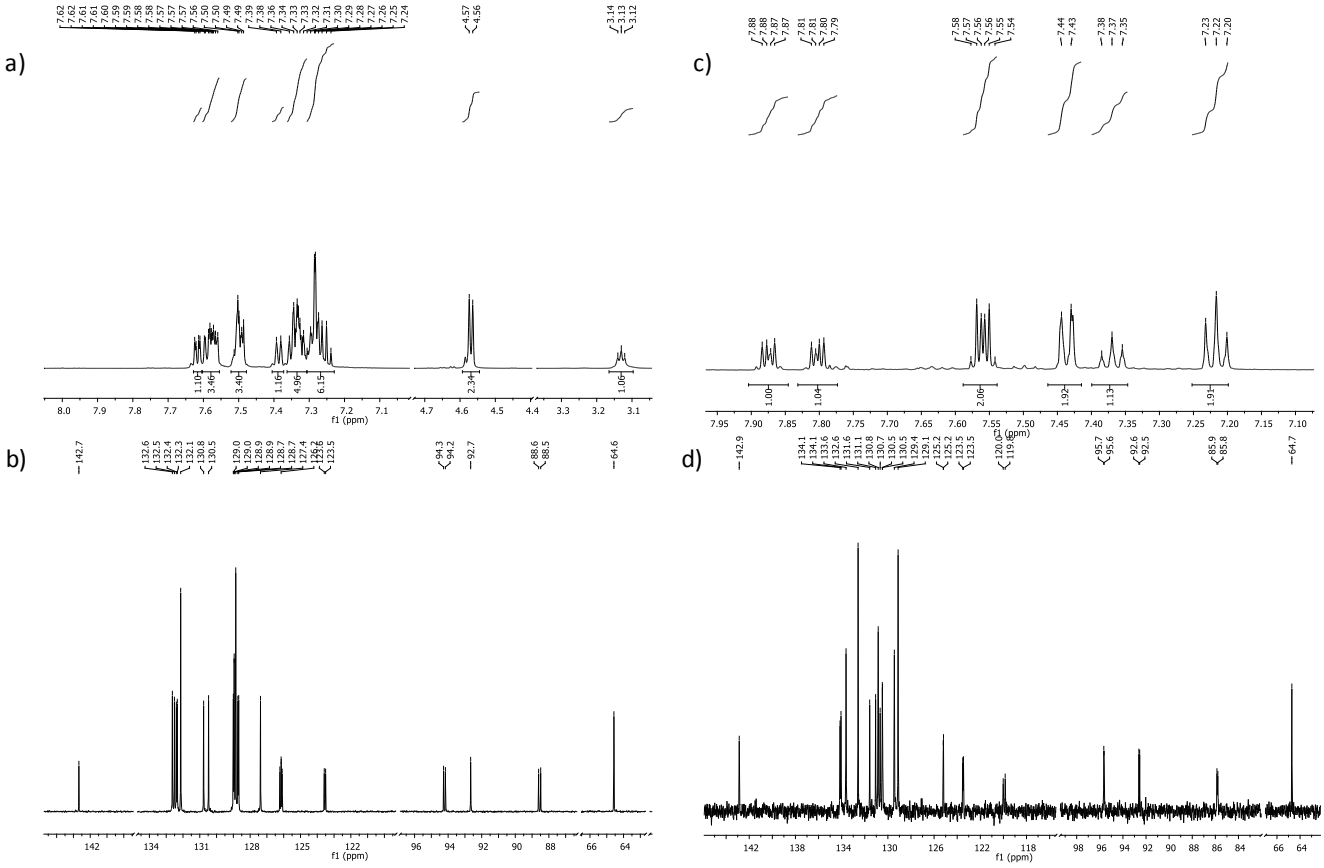
**Figure S3: Synthesis, analytical characterization, NMR spectra and titration curves for the monohydroxylated ligand 17.**

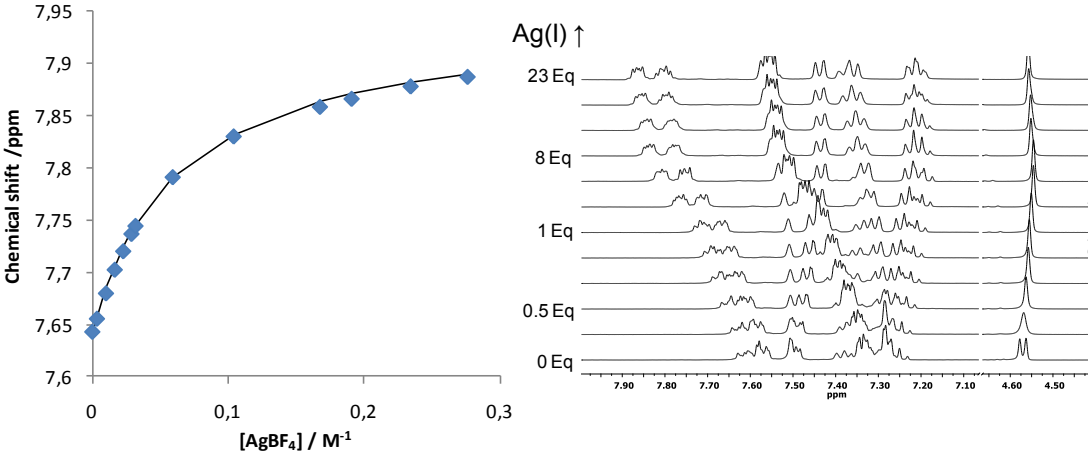



***Compound* 17** was prepared from **I** (300 mg, 1.15 mmol) and 1-ethynyl-2-(phenylethynyl)benzene **II** (436 mg, 1.26 mmol) according to previously described *GP2* to give **5** in 53 % yield (315 mg) as a pale yellow syrup. $^{1}$H NMR (600 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.64 – 7.55 (m, 4H), 7.52 – 7.48 (m, 3H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.31 (m, 4H), 7.31 – 7.23 (m, 5H), 4.57 (d, *J* = 5.9 Hz, 2H), 3.13 (t, *J* = 5.8 Hz, 1H); $^{13}$C NMR (151 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 142.7 (C), 132.6 (CH), 132.5 (CH), 132.4 (CH), 132.3 (CH), 132.1 (CH), 130.8 (CH), 130.5 (CH), 129.0 (CH), 128.9 (CH), 128.70 (CH), 128.67 (CH), 127.4 (CH), 126.2 (C), 126.18 (C), 126.16 (C), 126.1 (C), 123.6 (C), 123.5 (C), 94.3 (C), 94.2 (C), 92.7 (C), 88.6 (C), 88.5 (C), 64.6 ($CH_2$), (some carbon signals were not observed); ESI-HRMS calculated for $C_{31}H_{21}O$ [M+H$^+$]: 409.1597, found: 409.1586.

**Complex 17·Ag(I):** $^{1}$H NMR (500 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 7.87 (dd, *J* = 6.0, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.59 – 7.54 (m, 4H), 7.43 (bd, *J* = 7.5 Hz, 4H),, 7.37 (t, *J* = 7.6 Hz, 2H), 7.22 (bt, *J* = 7.8 Hz, 4H). $^{13}$C NMR (126 MHz, 9:1 $CD_2Cl_2$:Acetone-$d_6$) δ 142.9 (C), 134.1 (CH), 134.1 (CH), 133.6 (CH), 132.6 (CH), 131.6 (CH), 131.1 (CH), 130.8 (CH), 130.7 (CH), 130.5 (CH), 130.5 (CH), 129.4 (CH), 129.1 (CH), 125.2 (C), 125.2 (C), 123.5 (C), 123.5 (C), 120.0 (C), 119.9 (C), 95.7 (C), 95.6 (C), 92.6 (C), 92.6 (C), 85.9 (C), 85.8 (C), 64.7 ($CH_2$).

$^{1}$H- and $^{13}$C-NMR spectra of **17** (a and b) and of the **17·Ag(I)** complex (c and d).



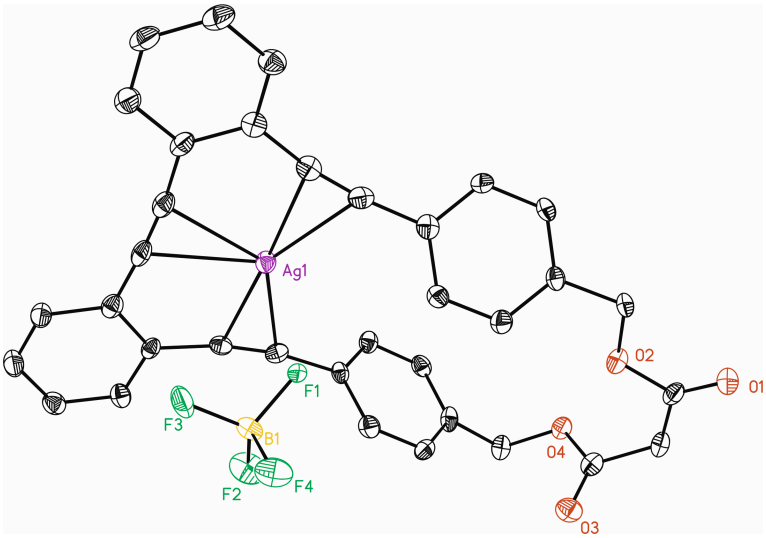



| Compound | Ka ($M^{-1}$) ± SD |
|---|---|
| **17** | 16.82±0.81 |

## X-ray crystallographic analyses

**Complex 1·Ag(I)**

Under inert argon atmosphere, $AgBF_4$ (19.5 mg, 0.1 mmol) was added to a solution of **1** (50.7 mg, 0.1 mmol) in dry $CH_2Cl_2$ (10 ml). The mixture was stirred for 4 h with the exclusion of light. A pale brown precipitate formed which was collected by vacuum filtration, dissolved in acetone, filtered through celite and then the solvent removed under reduced pressure to give **1·Ag(I)** as a pale brown solid (16.4 mg). The filtrate from the initial filtration was filtered through celite and then solvent removed under reduced pressure to give **1·Ag(I)** as a brown solid (40.2 mg). X-Ray quality crystals of **1·Ag(I)** were obtained by slow diffusion of hexane into a solution of the complex in dichloromethane. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.




Crystal data and structure refinement for **1·Ag(I)**

| | | |
|---|---|---|
| Empirical formula | C35 H22 Ag B F4 O4 | |
| Formula weight | 701.21 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | Cc | |
| Unit cell dimensions | a = 11.3153(9) Å | a= 90.00 °. |
| | b = 14.4329(9) Å | b = 90.232(4) °. |
| | c = 17.5533(11) Å | g = 90.00 °. |
| Volume | 2866.7(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.625 $Mg/m^3$ | |
| Absorption coefficient | 0.770 $mm^{-1}$ | |
| F(000) | 1408 | |
| Crystal size | 0.01 x 0.01 x 0.005 $mm^3$ | |

| | |
|---|---|
| Theta range for data collection | 2.29 to 30.53 °. |
| Index ranges | -16 <=h<=15 ,-20 <=k<=18 ,-24 <=l<=24 |
| Reflections collected | 11863 |
| Independent reflections | 5616 [R(int) = 0.0515 ] |
| Completeness to theta =30.53 ° | 87.5% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.9962 and 0.9923 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5616 / 232 / 496 |
| Goodness-of-fit on $F^2$ | 1.062 |
| Final R indices [I>2sigma(I)] | R1 = 0.0471 , wR2 = 0.1137 |
| R indices (all data) | R1 = 0.0594 , wR2 = 0.1212 |
| Flack parameter | x =-0.04(3) |
| Largest diff. peak and hole | 1.072 and -0.835 e.Å$^{-3}$ |

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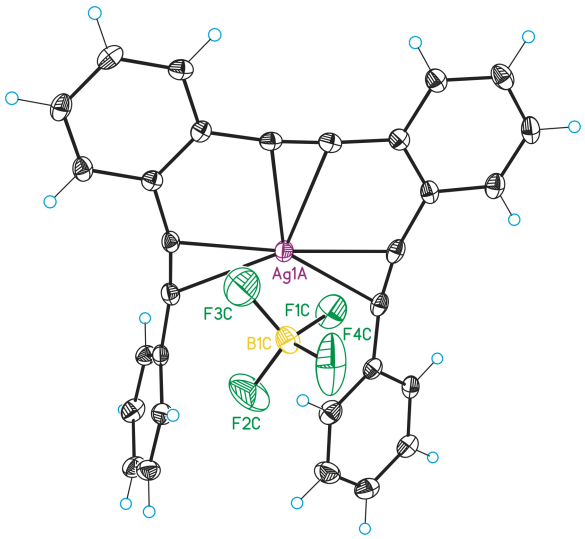
**8·Ag(I)**

Under inert argon atmosphere, $AgBF_4$ (19.5 mg, 0.100 mmol) was added to a solution of **8** (37.8 mg, 0.100 mmol) in dry $CH_2Cl_2$ (10 ml). The mixture was stirred overnight with the exclusion of light. The solution was filtered through celite and the filtrate evaporated to dryness to give **8·Ag(I)** as a pale brown solid (49.1 mg). X-Ray quality crystals were obtained by slow diffusion of pentane into a solution of the complex **8·Ag(I)** in dichloromethane. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.




Crystal data and structure refinement for **8·Ag(I)**

---

| | |
|---|---|
| Identification code | mo_AJ116_P21c |
| Empirical formula | C30 H18 Ag B F4 |

| | | |
|---|---|---|
| Formula weight | 573.12 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 17.2933(12) Å | a= 90.00 °. |
| | b = 27.625(2) Å | b = 104.778(2) °. |
| | c = 10.1403(7) Å | g = 90.00 °. |
| Volume | 4684.0(6) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.625 $Mg/m^3$ | |
| Absorption coefficient | 0.910 $mm^{-1}$ | |
| F(000) | 2288 | |
| Crystal size | 0.15 x 0.03 x 0.03 $mm^3$ | |
| Theta range for data collection | 1.22 to 29.96 °. | |
| Index ranges | -16 <=h<=24 ,-31 <=k<=38 ,-14 <=l<=13 | |
| Reflections collected | 28590 | |
| Independent reflections | 13454 [R(int) = 0.0361 ] | |
| Completeness to theta =29.96 ° | 98.9% | |
| Absorption correction | Empirical | |
| Max. and min. transmission | 0.9732 and 0.8756 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 13454 / 0 / 649 | |
| Goodness-of-fit on $F^2$ | 1.023 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0386 , wR2 = 0.0752 | |
| R indices (all data) | R1 = 0.0677 , wR2 = 0.0839 | |
| Largest diff. peak and hole | 0.730 and -0.642 $e.Å^{-3}$ | |

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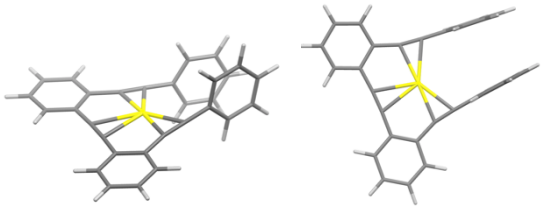
## Theoretical studies

All theoretical calculations were carried out using the M06 functional with the 6–31G* basis set for the ligands and the LANL2DZ relativistic effective core potential basis set for the Ag(I) ion as implemented in the Gaussian 09 program[9]

*XYZ Coordinates of all the calculated structures*



**Complex 8·Ag(I)** = AgC30H18

| | | | |
|---|---|---|---|
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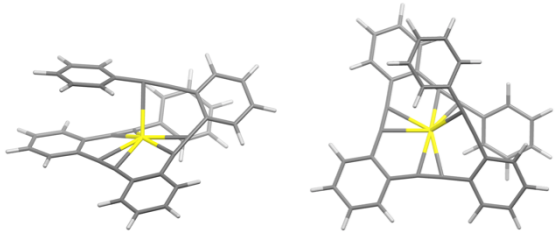
| C | -2.719431000 | 1.110322000 | 2.041971000 |
| H | -3.015716000 | 0.755530000 | 3.026767000 |
| C | -1.395724000 | 1.449014000 | 1.801515000 |
| H | -0.646785000 | 1.367486000 | 2.587788000 |
| C | -1.016856000 | 1.921776000 | 0.535591000 |
| C | 0.341286000 | 2.306096000 | 0.301812000 |
| C | 1.508697000 | 2.681249000 | 0.154017000 |
| C | 2.731947000 | 3.432420000 | 0.105562000 |
| C | 2.687885000 | 4.804506000 | 0.374839000 |
| H | 1.728797000 | 5.266925000 | 0.598572000 |
| C | 3.850122000 | 5.562198000 | 0.357094000 |
| H | 3.801187000 | 6.628131000 | 0.566626000 |
| C | 5.073589000 | 4.959370000 | 0.073257000 |
| H | 5.984807000 | 5.552976000 | 0.059670000 |
| C | 5.137355000 | 3.600274000 | -0.196947000 |
| H | 6.089874000 | 3.125280000 | -0.421570000 |
| C | 3.974074000 | 2.819704000 | -0.188903000 |
| C | 4.071043000 | 1.426186000 | -0.477513000 |
| C | 4.224230000 | 0.236879000 | -0.738831000 |
| C | 4.495938000 | -1.131628000 | -1.034988000 |
| C | 3.455112000 | -2.069460000 | -1.243217000 |
| C | 2.072005000 | -1.685886000 | -1.187593000 |
| C | 0.839212000 | -1.628773000 | -1.236510000 |
| C | -0.586388000 | -1.594741000 | -1.361684000 |
| C | -1.164687000 | -1.239854000 | -2.590107000 |
| H | -0.520882000 | -0.994066000 | -3.433349000 |
| C | -2.545897000 | -1.222631000 | -2.721159000 |
| H | -2.994437000 | -0.958194000 | -3.676369000 |

[9] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, F. Izmaylov, J. Bloino, G. Zeng, J. L. Sonneberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, R. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2010**.

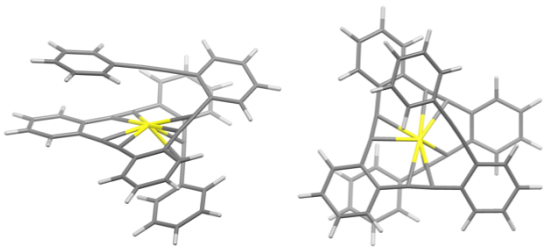
| | | | |
|---|---|---|---|
| C | -3.353208000 | -1.552982000 | -1.635158000 |
| C | -2.782683000 | -1.898860000 | -0.411950000 |
| H | -3.417304000 | -2.155250000 | 0.433935000 |
| C | -1.403016000 | -1.920504000 | -0.268379000 |
| H | -0.944059000 | -2.191154000 | 0.681544000 |
| C | 3.777713000 | -3.401522000 | -1.524070000 |
| H | 2.972690000 | -4.116136000 | -1.682184000 |
| C | 5.103886000 | -3.803922000 | -1.597535000 |
| H | 5.339189000 | -4.843394000 | -1.813911000 |
| C | 6.128105000 | -2.881232000 | -1.395092000 |
| H | 7.166936000 | -3.198095000 | -1.452263000 |
| C | 5.828214000 | -1.555809000 | -1.117394000 |
| H | 6.623737000 | -0.831532000 | -0.956616000 |
| C | -1.972010000 | 2.039293000 | -0.485556000 |
| H | -1.668075000 | 2.406367000 | -1.465017000 |
| C | -3.292656000 | 1.698026000 | -0.232167000 |
| H | -4.035580000 | 1.793514000 | -1.021514000 |
| Ag | 1.725903000 | 0.487478000 | -0.493525000 |
| H | -4.436374000 | -1.542615000 | -1.742601000 |
| H | -4.706103000 | 0.979427000 | 1.223375000 |



**Complex 9·Ag(I)** = AgC38H22

| | | | |
|---|---|---|---|
| C | 1.038405000 | -1.567830000 | -1.371896000 |
| C | -0.166288000 | -1.763062000 | -1.505859000 |
| C | -1.568082000 | -2.028696000 | -1.602747000 |
| C | -2.083916000 | -3.227371000 | -1.088321000 |
| H | -1.404187000 | -3.956445000 | -0.649852000 |
| C | -3.448762000 | -3.472223000 | -1.142246000 |
| H | -3.845627000 | -4.404142000 | -0.744712000 |
| C | -4.307149000 | -2.531304000 | -1.706744000 |
| C | -3.800046000 | -1.343741000 | -2.229931000 |
| H | -4.471422000 | -0.612115000 | -2.674978000 |
| C | -2.437757000 | -1.086501000 | -2.174926000 |
| H | -2.031162000 | -0.161212000 | -2.585215000 |
| H | -5.376646000 | -2.728383000 | -1.747179000 |
| C | 4.589262000 | -2.659009000 | -1.404249000 |
| C | 3.204824000 | -2.671109000 | -1.496469000 |
| H | 2.674415000 | -3.589108000 | -1.742253000 |
| C | 2.463699000 | -1.504310000 | -1.278456000 |
| C | 3.144703000 | -0.304853000 | -0.949816000 |
| C | 2.446300000 | 0.915615000 | -0.704488000 |
| C | 1.917015000 | 2.006192000 | -0.505055000 |
| C | 1.421427000 | 3.336222000 | -0.345315000 |
| C | 2.313926000 | 4.404679000 | -0.507571000 |
| H | 3.355552000 | 4.187669000 | -0.734953000 |
| C | 1.877910000 | 5.715912000 | -0.392044000 |
| H | 2.584945000 | 6.531234000 | -0.526093000 |

| | | | |
|---|---|---|---|
| C | 0.540057000 | 5.985507000 | -0.110796000 |
| H | 0.195031000 | 7.013014000 | -0.022343000 |
| C | -0.358069000 | 4.943049000 | 0.058889000 |
| H | -1.403070000 | 5.145816000 | 0.283905000 |
| C | 0.062005000 | 3.611087000 | -0.051734000 |
| C | -0.911124000 | 2.581769000 | 0.150702000 |
| C | -1.879038000 | 1.868460000 | 0.411372000 |
| C | 4.542889000 | -0.311148000 | -0.868119000 |
| H | 5.058956000 | 0.614357000 | -0.620648000 |
| C | 5.259062000 | -1.477907000 | -1.092894000 |
| H | 6.344429000 | -1.465238000 | -1.024918000 |
| Ag | 0.041941000 | 0.394042000 | -0.251965000 |
| H | 5.148335000 | -3.575121000 | -1.581315000 |
| C | -3.028157000 | 1.086767000 | 0.731702000 |
| C | -2.901610000 | -0.182080000 | 1.356296000 |
| C | -1.612796000 | -0.693796000 | 1.680990000 |
| C | -0.491368000 | -1.099234000 | 1.939703000 |
| C | 0.849015000 | -1.539084000 | 2.164182000 |
| C | 1.821772000 | -0.620184000 | 2.591494000 |
| H | 1.523861000 | 0.403702000 | 2.818482000 |
| C | 3.144308000 | -1.021021000 | 2.725008000 |
| H | 3.892926000 | -0.307594000 | 3.063934000 |
| C | 3.509180000 | -2.333705000 | 2.433763000 |
| C | 2.547261000 | -3.250846000 | 2.014648000 |
| H | 2.833037000 | -4.277232000 | 1.792104000 |
| C | 1.221425000 | -2.861916000 | 1.883651000 |
| H | 0.462637000 | -3.570418000 | 1.553919000 |
| C | -4.056274000 | -0.918075000 | 1.637601000 |
| H | -3.953093000 | -1.894037000 | 2.107770000 |
| C | -5.311449000 | -0.410824000 | 1.326498000 |
| H | -6.199644000 | -0.993808000 | 1.560476000 |
| C | -5.434863000 | 0.838561000 | 0.723547000 |
| H | -6.418509000 | 1.237692000 | 0.486603000 |
| C | -4.301087000 | 1.580998000 | 0.423974000 |
| H | -4.388906000 | 2.556200000 | -0.051122000 |
| H | 4.547238000 | -2.644735000 | 2.534709000 |

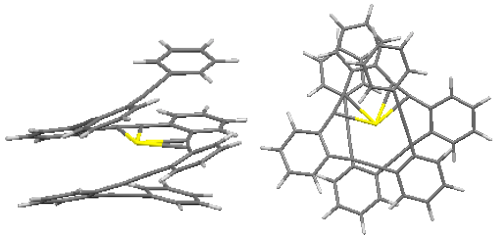


**Complex 10·Ag(I)** = AgC46H26

| | | | |
|---|---|---|---|
| C | 1.657503000 | 1.770220000 | 0.110282000 |
| C | 2.251370000 | 0.829477000 | -0.413359000 |
| C | 3.107996000 | -0.164260000 | -0.979020000 |
| C | 4.484806000 | 0.099392000 | -0.994801000 |
| H | 4.840982000 | 1.040914000 | -0.582572000 |
| C | 5.380951000 | -0.818073000 | -1.520462000 |
| H | 6.444858000 | -0.592051000 | -1.526399000 |
| C | 4.916974000 | -2.024148000 | -2.040862000 |
| H | 5.615571000 | -2.747125000 | -2.456693000 |
| C | 3.559840000 | -2.307975000 | -2.029538000 |

| | | | |
|---|---|---|---|
| H | 3.188172000 | -3.248951000 | -2.430513000 |
| C | 2.636820000 | -1.393880000 | -1.503469000 |
| C | 1.257763000 | -1.764957000 | -1.492920000 |
| C | 0.124954000 | -2.227804000 | -1.537856000 |
| Ag | -0.045955000 | -0.008220000 | -0.114663000 |
| C | -1.200187000 | -2.754559000 | -1.550381000 |
| C | -2.318398000 | -1.886125000 | -1.654051000 |
| C | -2.120759000 | -0.480715000 | -1.773619000 |
| C | -1.931696000 | 0.720412000 | -1.886817000 |
| C | -1.679313000 | 2.122832000 | -1.972664000 |
| C | -0.531216000 | 2.589930000 | -2.632945000 |
| H | 0.127115000 | 1.873210000 | -3.124159000 |
| C | -0.247554000 | 3.948460000 | -2.651647000 |
| H | 0.640732000 | 4.308173000 | -3.167329000 |
| C | -1.099929000 | 4.849061000 | -2.015427000 |
| C | -2.244532000 | 4.391638000 | -1.365503000 |
| H | -2.910859000 | 5.098540000 | -0.874105000 |
| C | -2.539052000 | 3.035455000 | -1.343851000 |
| H | -3.423211000 | 2.662740000 | -0.828119000 |
| C | -3.608612000 | -2.422785000 | -1.612163000 |
| H | -4.459328000 | -1.747526000 | -1.682815000 |
| C | -3.798557000 | -3.792381000 | -1.485653000 |
| H | -4.808479000 | -4.196370000 | -1.460787000 |
| C | -2.701686000 | -4.646632000 | -1.394242000 |
| H | -2.851163000 | -5.719944000 | -1.299350000 |
| C | -1.412093000 | -4.132002000 | -1.422843000 |
| H | -0.551087000 | -4.793253000 | -1.345897000 |
| H | -0.871154000 | 5.913140000 | -2.026873000 |
| C | -0.996910000 | 1.860731000 | 1.441375000 |
| C | -1.818613000 | 0.969189000 | 1.610608000 |
| C | -2.737285000 | -0.110282000 | 1.759262000 |
| C | -4.116933000 | 0.119833000 | 1.732859000 |
| H | -4.480613000 | 1.141513000 | 1.637606000 |
| C | -5.008394000 | -0.940726000 | 1.827678000 |
| H | -6.078916000 | -0.748432000 | 1.809966000 |
| C | -4.533226000 | -2.245642000 | 1.944846000 |
| C | -3.167483000 | -2.494333000 | 1.975042000 |
| H | -2.788978000 | -3.510379000 | 2.069671000 |
| C | -2.253922000 | -1.439532000 | 1.891900000 |
| H | -5.232835000 | -3.075993000 | 2.015565000 |
| C | 0.161981000 | 5.374807000 | 1.740235000 |
| C | -0.610022000 | 4.226715000 | 1.835760000 |
| H | -1.586665000 | 4.255174000 | 2.315817000 |
| C | -0.153743000 | 3.006120000 | 1.320141000 |
| C | 1.112730000 | 2.959734000 | 0.683114000 |
| C | 1.878227000 | 4.131488000 | 0.599319000 |
| H | 2.848706000 | 4.086087000 | 0.108735000 |
| C | 1.410034000 | 5.326540000 | 1.122623000 |
| H | 2.020547000 | 6.223634000 | 1.049248000 |
| H | -0.210907000 | 6.310819000 | 2.150155000 |
| C | 0.362713000 | -1.791932000 | 1.989839000 |
| C | -0.849706000 | -1.668698000 | 1.925393000 |
| C | 3.886518000 | -0.768675000 | 2.551720000 |
| C | 2.499546000 | -0.748650000 | 2.538511000 |
| H | 1.948759000 | 0.124449000 | 2.889241000 |

| | | | |
|---|---|---|---|
| C | 1.784758000 | -1.861041000 | 2.063373000 |
| C | 2.481411000 | -2.996210000 | 1.623985000 |
| C | 3.869246000 | -3.008129000 | 1.645294000 |
| H | 4.407994000 | -3.888745000 | 1.301229000 |
| C | 4.572582000 | -1.894619000 | 2.100683000 |
| H | 5.660893000 | -1.907029000 | 2.110283000 |
| H | 4.435750000 | 0.095884000 | 2.920095000 |
| H | 1.920611000 | -3.855746000 | 1.258653000 |



**Complex 11·Ag(I)** = AgC54H30

| | | | |
|---|---|---|---|
| C | 0.998045000 | -2.250330000 | -1.816025000 |
| C | -0.180102000 | -2.209768000 | -2.122285000 |
| C | -1.556705000 | -2.167573000 | -2.479671000 |
| C | -2.032932000 | -1.152871000 | -3.323917000 |
| H | -1.331085000 | -0.417484000 | -3.716541000 |
| C | -3.381335000 | -1.097842000 | -3.648934000 |
| H | -3.746579000 | -0.313267000 | -4.309037000 |
| C | -4.263226000 | -2.047388000 | -3.138065000 |
| C | -3.795334000 | -3.059758000 | -2.302153000 |
| H | -4.486150000 | -3.802783000 | -1.907741000 |
| C | -2.448767000 | -3.126149000 | -1.975816000 |
| H | -2.068003000 | -3.908896000 | -1.320687000 |
| H | -5.319556000 | -2.002410000 | -3.396847000 |
| C | -0.942348000 | -1.946389000 | 1.219755000 |
| C | -1.864652000 | -1.250636000 | 0.809201000 |
| C | -3.057613000 | -0.591251000 | 0.386586000 |
| C | -4.284703000 | -1.163915000 | 0.749767000 |
| H | -4.278045000 | -2.070031000 | 1.353143000 |
| C | -5.483081000 | -0.589506000 | 0.355946000 |
| H | -6.424129000 | -1.049089000 | 0.650442000 |
| C | -5.478840000 | 0.572617000 | -0.412680000 |
| H | -6.416529000 | 1.028114000 | -0.723733000 |
| C | -4.276156000 | 1.152042000 | -0.785340000 |
| H | -4.262794000 | 2.058177000 | -1.388589000 |
| C | -3.053316000 | 0.583237000 | -0.402271000 |
| C | -1.856282000 | 1.244877000 | -0.809713000 |
| C | -0.931885000 | 1.942419000 | -1.213030000 |
| C | 1.865135000 | -1.255430000 | 1.790447000 |
| C | 2.426211000 | -0.171320000 | 1.738998000 |
| C | 3.087554000 | 1.076866000 | 1.576285000 |
| C | 4.467153000 | 1.112355000 | 1.339231000 |
| H | 5.027879000 | 0.178826000 | 1.359711000 |
| C | 5.099492000 | 2.314404000 | 1.055241000 |
| H | 6.171823000 | 2.332176000 | 0.872369000 |
| C | 4.361049000 | 3.496513000 | 1.002550000 |
| C | 2.996646000 | 3.482576000 | 1.257052000 |
| H | 2.414047000 | 4.402252000 | 1.226999000 |
| C | 2.343456000 | 2.282807000 | 1.559032000 |

| | | | |
|---|---|---|---|
| H | 4.855966000 | 4.438032000 | 0.773017000 |
| C | 1.823338000 | -4.913786000 | 2.408205000 |
| C | 2.253276000 | -3.600298000 | 2.296460000 |
| H | 3.289037000 | -3.336688000 | 2.501763000 |
| C | 1.367552000 | -2.583776000 | 1.914125000 |
| C | 0.018793000 | -2.913665000 | 1.639261000 |
| C | -0.396616000 | -4.247495000 | 1.757344000 |
| H | -1.436380000 | -4.491876000 | 1.546939000 |
| C | 0.495264000 | -5.238991000 | 2.137542000 |
| H | 0.154049000 | -6.268205000 | 2.222806000 |
| H | 2.525835000 | -5.687805000 | 2.709457000 |
| C | -0.229853000 | 2.208876000 | 2.128867000 |
| C | 0.949523000 | 2.252673000 | 1.829108000 |
| C | -3.432045000 | 1.075136000 | 3.636989000 |
| C | -2.082190000 | 1.140216000 | 3.320311000 |
| H | -1.377182000 | 0.410628000 | 3.717968000 |
| C | -1.608134000 | 2.157412000 | 2.477722000 |
| C | -2.504659000 | 3.108411000 | 1.967380000 |
| C | -3.852773000 | 3.031796000 | 2.284918000 |
| H | -4.546847000 | 3.768851000 | 1.885027000 |
| C | -4.318228000 | 2.016927000 | 3.119152000 |
| H | -5.375636000 | 1.964660000 | 3.372084000 |
| H | -3.795204000 | 0.288957000 | 4.296395000 |
| H | -2.126099000 | 3.893567000 | 1.313778000 |
| Ag | 0.226553000 | -0.011412000 | -0.017114000 |
| C | 0.026539000 | 2.914898000 | -1.627244000 |
| C | 1.376774000 | 2.592574000 | -1.904390000 |
| C | 1.882803000 | 1.267084000 | -1.783716000 |
| C | 2.452284000 | 0.187360000 | -1.729254000 |
| C | 3.123924000 | -1.054537000 | -1.559248000 |
| C | 2.390970000 | -2.267223000 | -1.539032000 |
| C | 3.053326000 | -3.459471000 | -1.226939000 |
| H | 2.479027000 | -4.384207000 | -1.194515000 |
| C | 4.416507000 | -3.459249000 | -0.965435000 |
| C | 5.144398000 | -2.270789000 | -1.021624000 |
| H | 6.215866000 | -2.277555000 | -0.833136000 |
| C | 4.502559000 | -1.076135000 | -1.315686000 |
| H | 5.054660000 | -0.137723000 | -1.340310000 |
| C | 2.257260000 | 3.615056000 | -2.282955000 |
| H | 3.294523000 | 3.357681000 | -2.488624000 |
| C | 1.820931000 | 4.926868000 | -2.389251000 |
| H | 2.519547000 | 5.705517000 | -2.687458000 |
| C | 0.491458000 | 5.244523000 | -2.116372000 |
| H | 0.145155000 | 6.272404000 | -2.197348000 |
| C | -0.395180000 | 4.247251000 | -1.739492000 |
| H | -1.435864000 | 4.485837000 | -1.526836000 |
| H | 4.919084000 | -4.394664000 | -0.727759000 |

# Photophysical studies

## Absorption and emission studies

**Figure S4:** Normalized absorption (dotted line) and emission (solid line, excitation wavelenght between parenthesis) spectra of compounds **12** ($2.7 \cdot 10^{-5}$M) and **13** ($4.4 \cdot 10^{-5}$M)

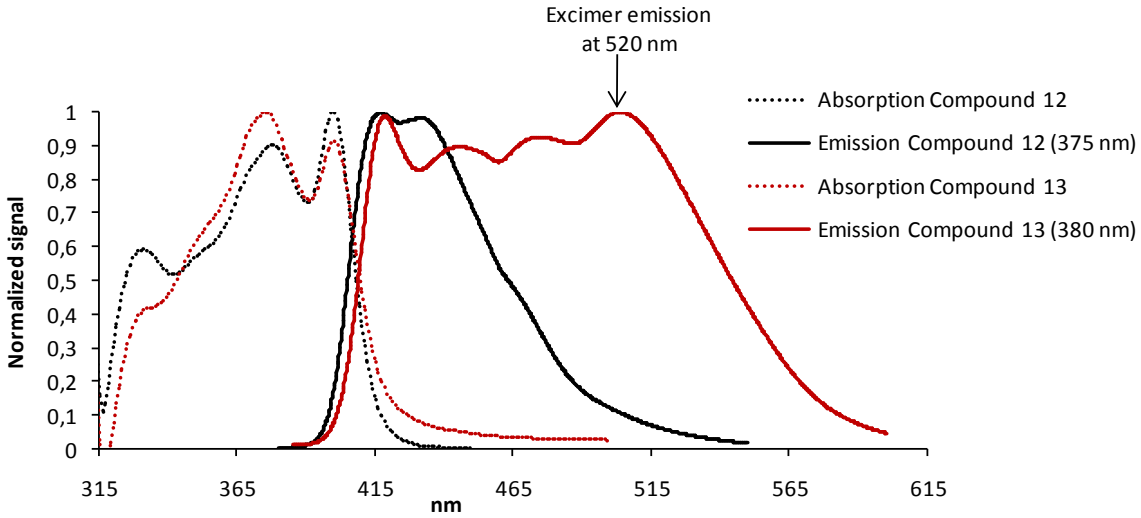



**Figure S5**: Normalized absorption and fluorescence spectra (375 nm) registered upon stepwise addition of $AgBF_4$ to a solution of **12** (measured at $2.7 \cdot 10^{-5}$M, room temperature)

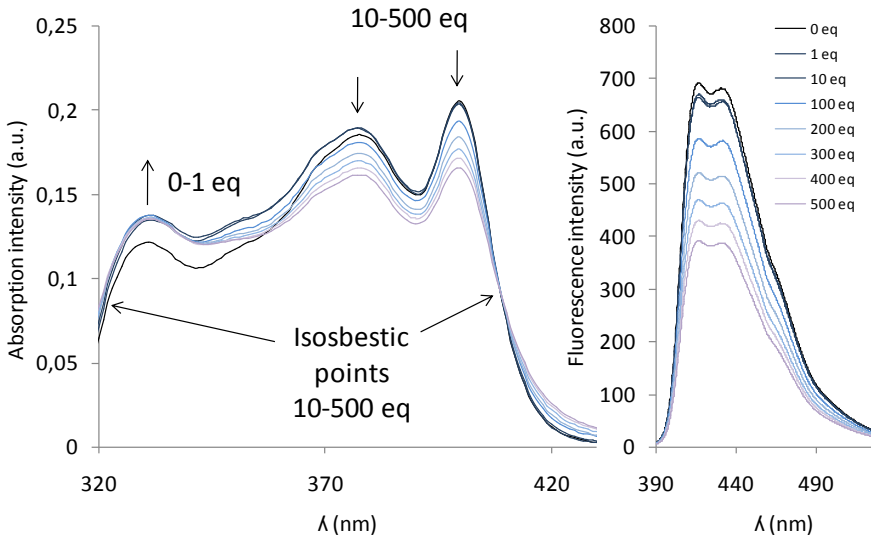
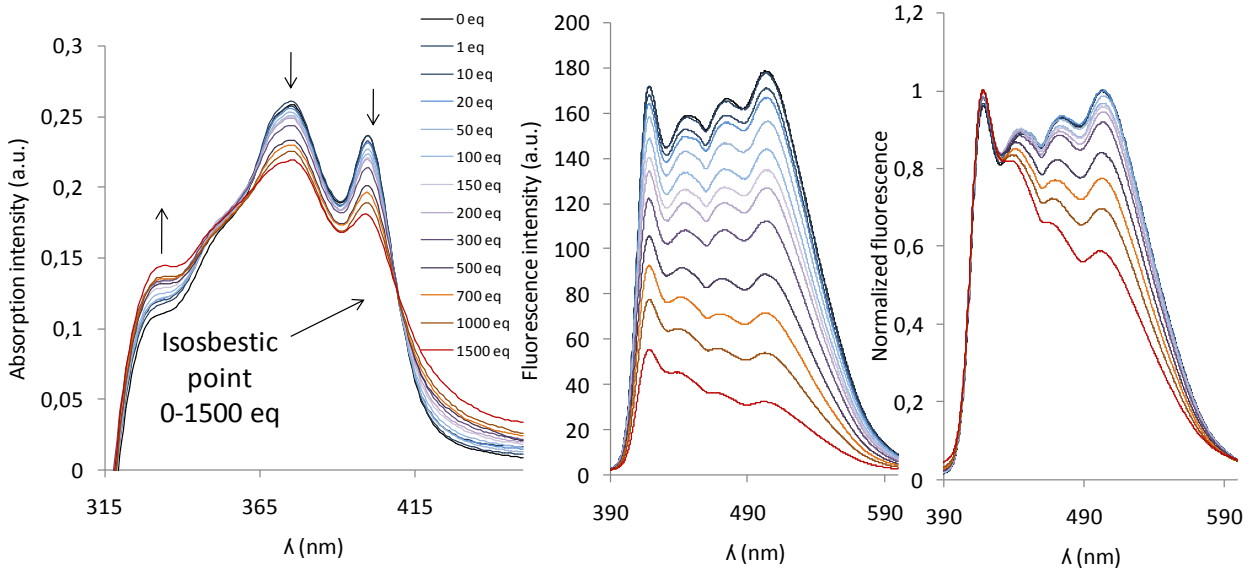



**Figure S6**: Normalized absorption and fluorescence spectra (380 nm) registered upon stepwise addition of $AgBF_4$ to a solution of **13** (measured at $4.4 \cdot 10^{-5}$M, room temperature). Normalized fluorescence spectra (right) highlight a significant ratiometric change at the longer wavelength bands along the titration of **13** with Ag(I).




**Fluorescence quantum yield determinations**

The fluorescence quantum yields Φ were computed according to the following expression:

$$\Phi_S = \Phi_R \times \frac{F_S}{F_R} \times \frac{1-10^{-A_R(\lambda_{ex})}}{1-10^{-A_S(\lambda_{ex})}} \times \frac{n_S^2}{n_R^2}$$

where subscripts S and R refer respectively to sample and reference fluorophore (quinine sulfate, 0.1 M $H_2SO_4$) with known quantum yield (0.54), *F* stands for the *corrected*, integrated fluorescence spectra, $A(\lambda_{ex})$ denotes the absorbance at the used excitation wavelength $\lambda_{ex}$ and *n* represents the refractive index of the solvent.

To minimize inner filter effects, the absorbance at the excitation wavelength $\lambda_{ex}$ was kept under 0.1. All measurements were done on non-degassed samples at room temperature. The averages and standard uncertainties of Φ are computed from independent Φ measurements (two different concentrations of sample × two different concentrations of reference × two different excitation wavelengths $\lambda_{ex}$).

**Time-resolved fluorescence measurements (Photokinetical study)**

Fluorescence decay traces were recorded in the single photon timing (SPT) mode using a FluoTime 200 fluorometer (PicoQuant, GmbH). Briefly, the samples were excited by a 405 nm Picosecond Pulsed Diode Laser (Edinburgh EPL405) with a 10 MHz repetition rate. The full width at half maximum of the laser pulse was ~ 90 ps. The fluorescence was collected after crossing through a polarizer set at the magic angle, 2-mm slits and a 2 nm bandwidth monochromator. Fluorescence decay histograms were collected using a TimeHarp200 board, with a time increment per channel of 36 ps, at three or more different wavelengths. The histograms of the instrument response function (IRF) was determined using LUDOX scatterer, and sample decays were recorded until they typically reached $2 \times 10^4$ counts in the peak channel. Time-resolved emission spectroscopy (TRES) was performed using the same configuration; collecting fluorescence decay traces every 2 nm (from 420 to 510 nm) during a fixed amount of time to maintain the overall intensity information.

Time resolved fluorescence decay traces were deconvoluted from the signal and fitted using FluoFit 4.4 package (Picoquant GmbH). In all cases, fluorescence decay traces were recorded at different emission wavelengths, and all decay traces were fitted globally with the decay times linked as shared parameters, whereas the pre-exponential factors were local adjustable parameters. The experimental decay traces were fitted to multi-exponential functions via a Levenberg-Marquard algorithm-based nonlinear least-squares error minimization deconvolution method. The quality of fittings was judged by the reduced chi-squared method, $\chi^2$, the weighted residuals and the correlation functions. The latter two were checked for random distributions.

For the TRES analysis and the estimation of the species-associated emission spectra (SAEMS), the same fitting procedure was performed. Then, SAEMS of each species *i* at any given emission wavelength ($SAEMS_i(\lambda_{em})$) is given by the fluorescence

intensity emitted by the species *i* ($A_{i,\lambda em} \times \tau_i$), normalized by the total intensity and corrected for the different detection sensitivity using the total intensity of the steady-state spectrum ($I_{ss,\lambda em}$):

$$SAEMS_i(\lambda_{em}) = \frac{A_{i,\lambda em} \times \tau_i}{\sum_i A_{i,\lambda em} \times \tau_i} \cdot I_{ss,\lambda em}$$

With the SAEMS, the approximate contribution of each species to the total spectrum is estimated. However, this is just an approximation because the promoted amount of each of the species to the excited state is unknown, as the molar absorption coefficients of each form are not separately accessible. Therefore, the approximated contribution of each form, assumes equal excitation rate for all the species.

**Figure S7**: Fluorescence decays registered at 420 nm for **13**

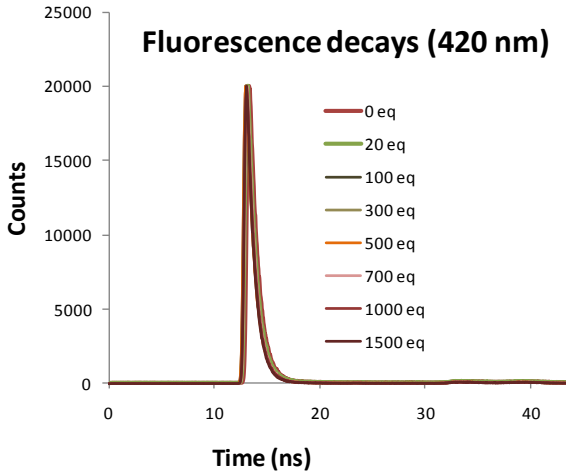
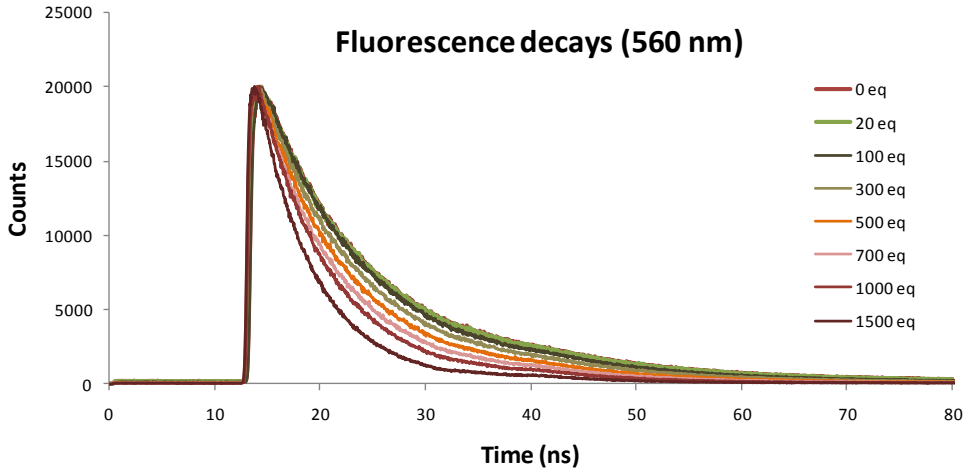
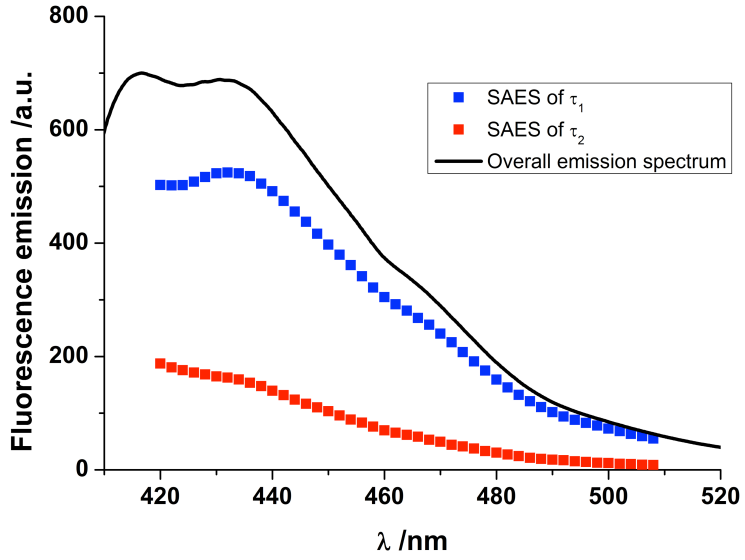



**Figure S8**: Fluorescence decays registered at 560 nm for **13**




Time-resolved emission spectroscopy (TRES) of compound **12** showed the presence of two different emissive species. The species-associated emission spectra (SAEMS) provide the spectral profile of each of the forms associated to each one of the decay times. The longest lifetime, $\tau_1$, (blue dots) shows a higher emission density in the spectral the shoulder at 440 nm, whereas the short decay time, $\tau_2$, (red dots) is more prominent at the blue emission wavelengths (peak at 420 nm). This spectral distribution suggests that the longest lifetime, $\tau_1$, corresponds to the folded species as the π-stacking causes a batochromic shift. Comparing the SAEMS with the overall steady-state emission spectra (black line) allowed to estimate an approximate 70%:30% ratio for the folded:unfolded forms. Note that this estimation takes into account the different emission efficiency of each form, as their quantum yield is proportional to the lifetime, but it does not take into account the different excitation efficiencies, as the individual extinction coefficients are not known. The estimation assumes equal, at least very similar, extinction coefficients of the two species at the excitation wavelength used.

**Figure S9**. SAEMS decomposition of **12**




**Estimation of the excited-state folding kinetic rate**

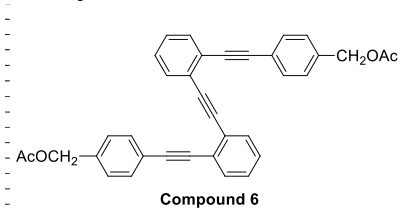
The kinetics of the excited-state folding reaction can be accessible through the fluorescence decay times. Indeed, the rate of the pyrene excimer formation, $k_f$, can be directly correlated with the excited-state folding kinetic constant. This rate constant can be obtained via the shortest decay time, $\tau_3$, by solving the kinetic differential equations:[39] $k_f = 1/\tau_3 - 1/\tau_{ref}$, where $\tau_{ref}$ is the fluorescence of a reference pyrene monomer, in the absence of excited-state reaction. We used **12** as the reference, because of its structural similarity with **13**, but lacking the second pyrene moiety, so the intramolecular excimer formation is avoided. The average fluorescence lifetime $\tau_{ref}$ was 2.36±0.09 ns. In the absence of Ag(I), the value of $k_f$ is $(9.8\pm0.3)\times10^8$ $s^{-1}$, and represents one of the few examples of experimentally determined kinetic folding constant in OPE-based foldamers.[40] At increasing Ag(I) concentrations, the value of $\tau_3$ provides the estimation of the excited-state folding rate. As expected, the presence of Ag(I) favors the excited-state folding process, and the $k_f$ value increases (Figure 10c).

**CD titrations**

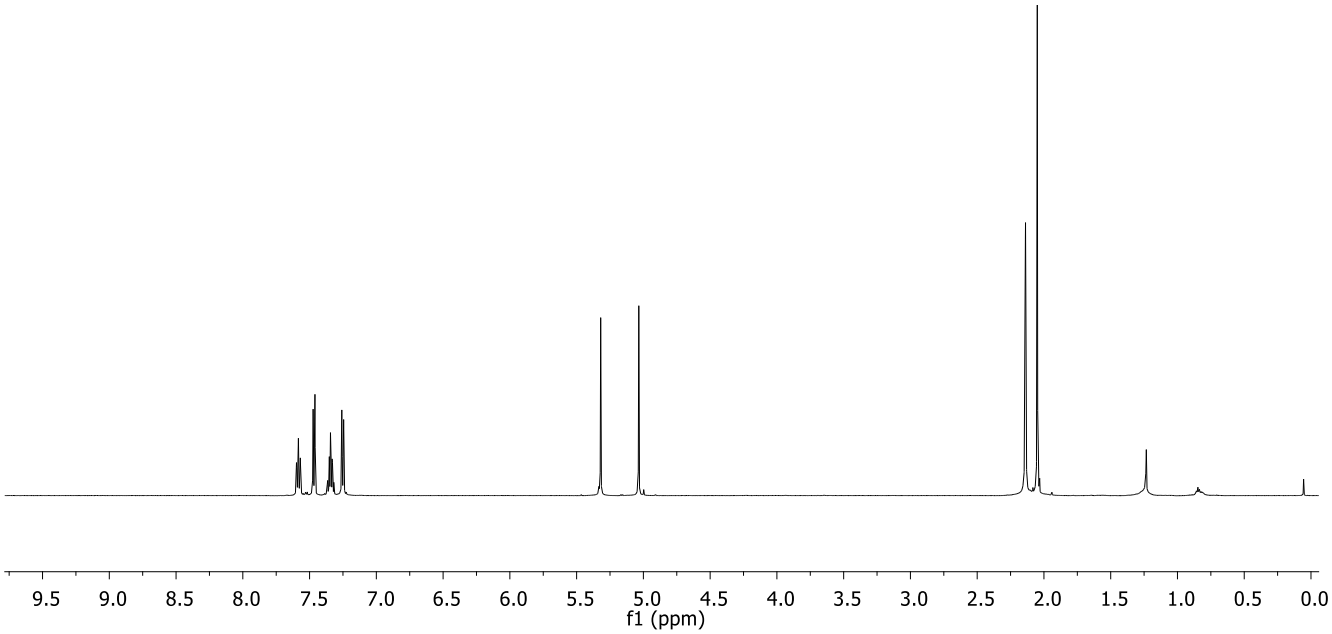
The experiments were conducted from stock solutions of the ligands ($10^{-4}$M) in $CH_2Cl_2$/Acetone (v/v, 9:1). Two or three solutions of different concentrations of the $AgBF_4$ were prepared in $CD_2Cl_2$/Acetone (v/v, 9:1). A small portion of the ligand was transferend to a cuvette and diluted with the solvent mixture to $10^{-5}$-$10^{-6}$M. After taking the initial spectra, small portions (from 1-100 µL) of the silver solution were added and the spectra recorded after each addition.

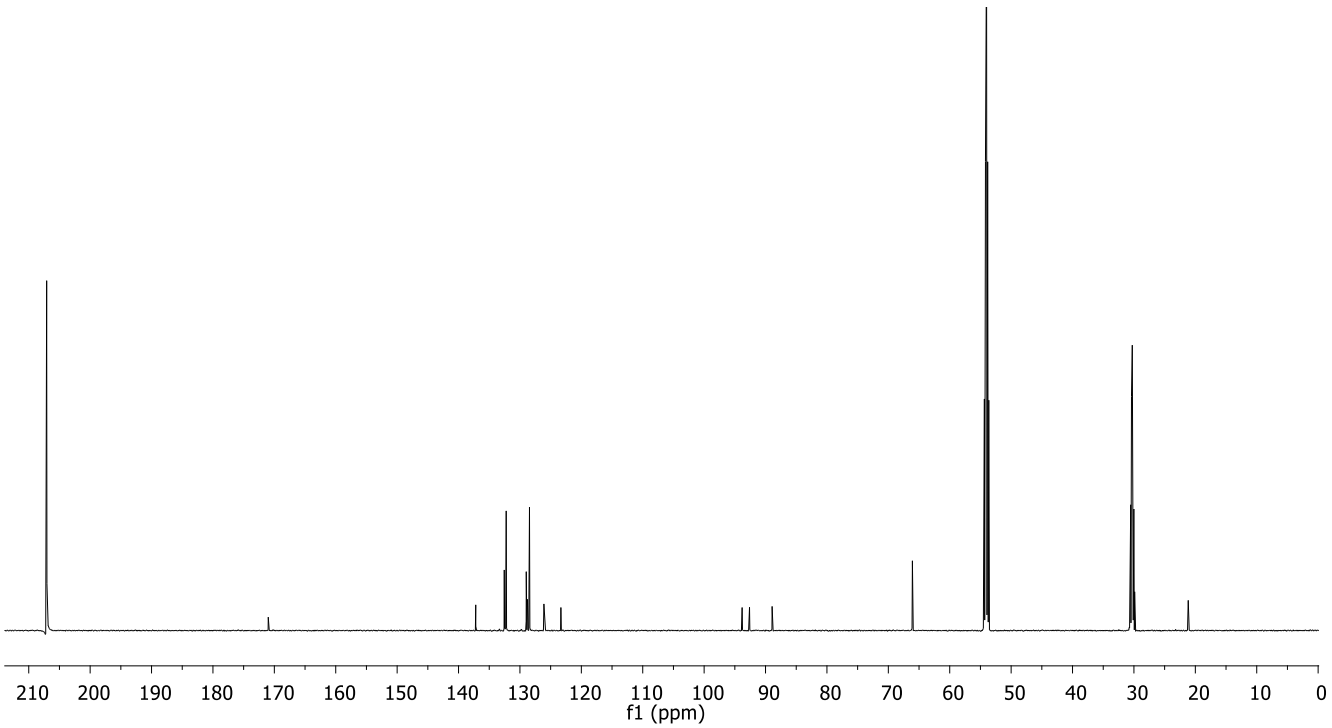
## $^{1}$H- and $^{13}$C-NMR spectra

## Compound 6:



Compound 6



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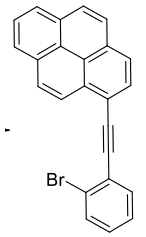
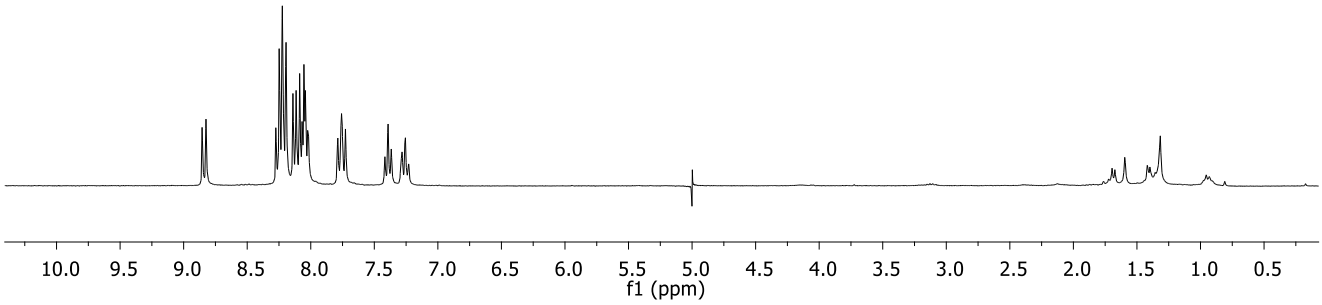
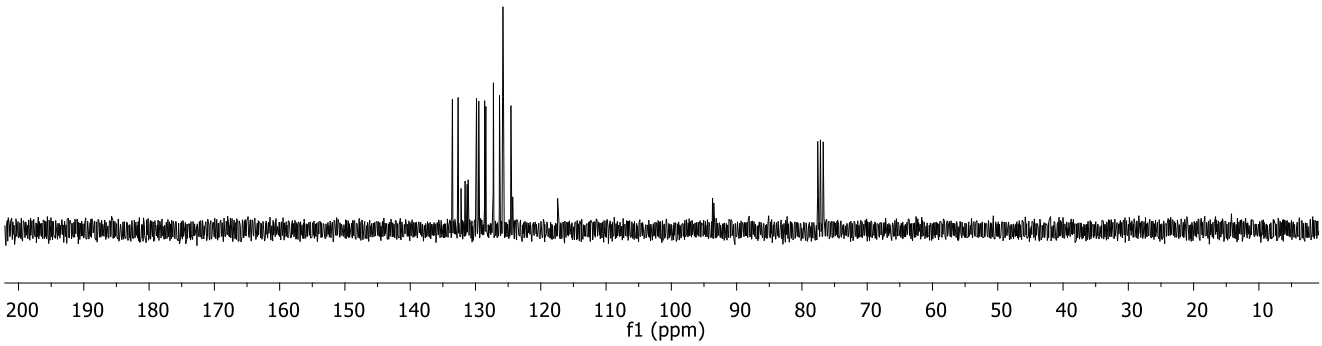

Br

I


10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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f1 (ppm)

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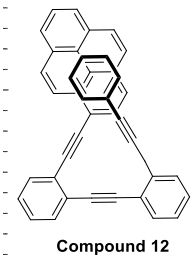
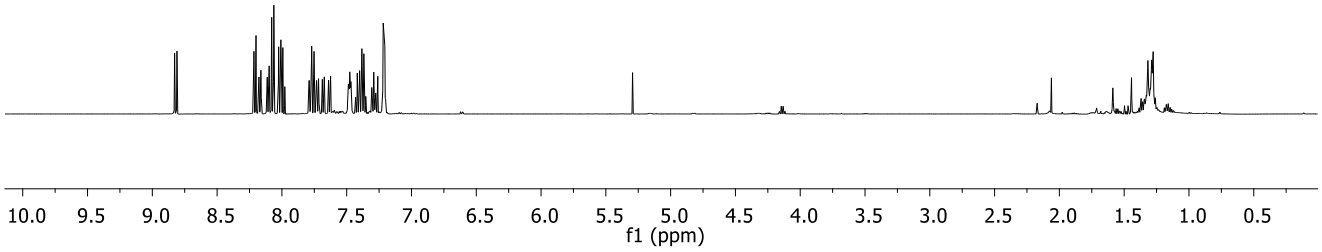
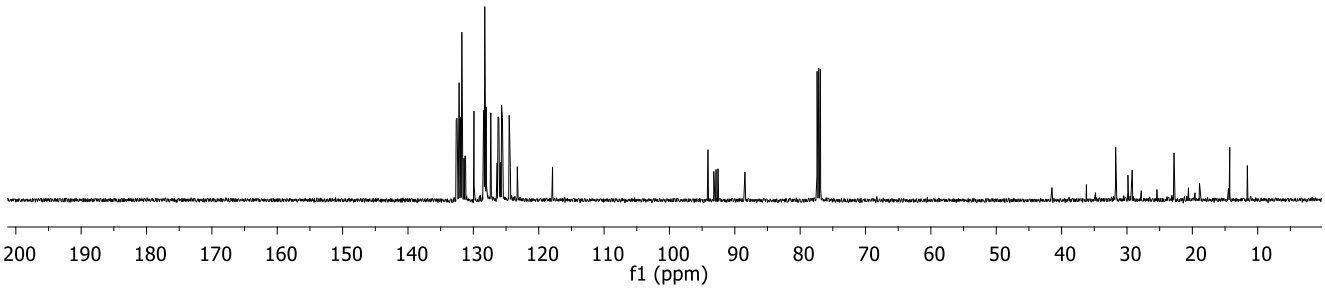


Compound 12



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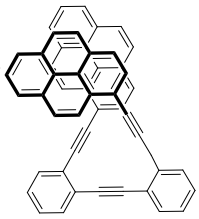
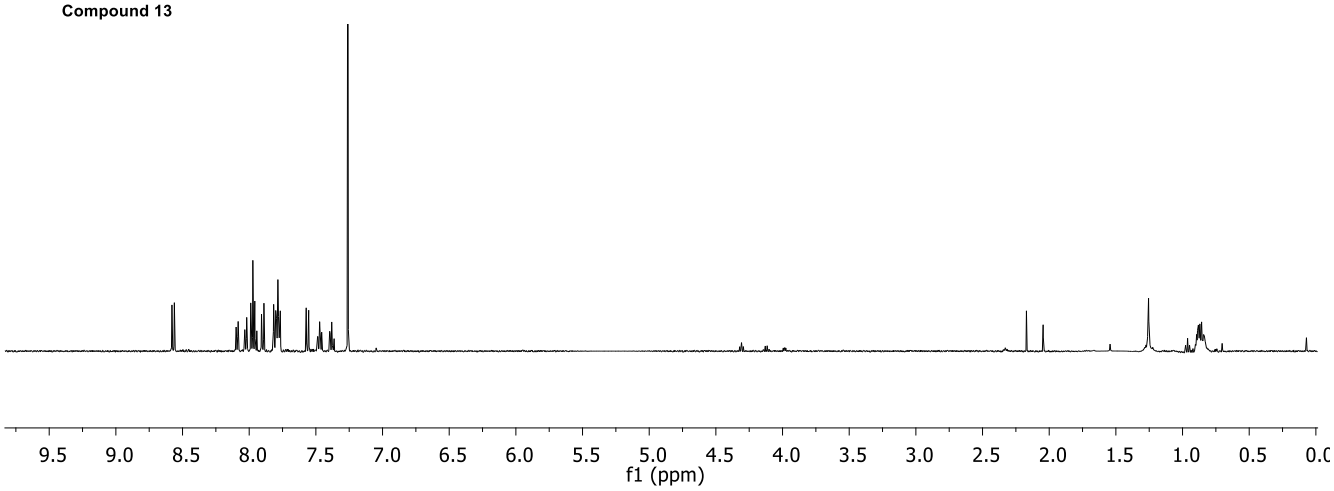
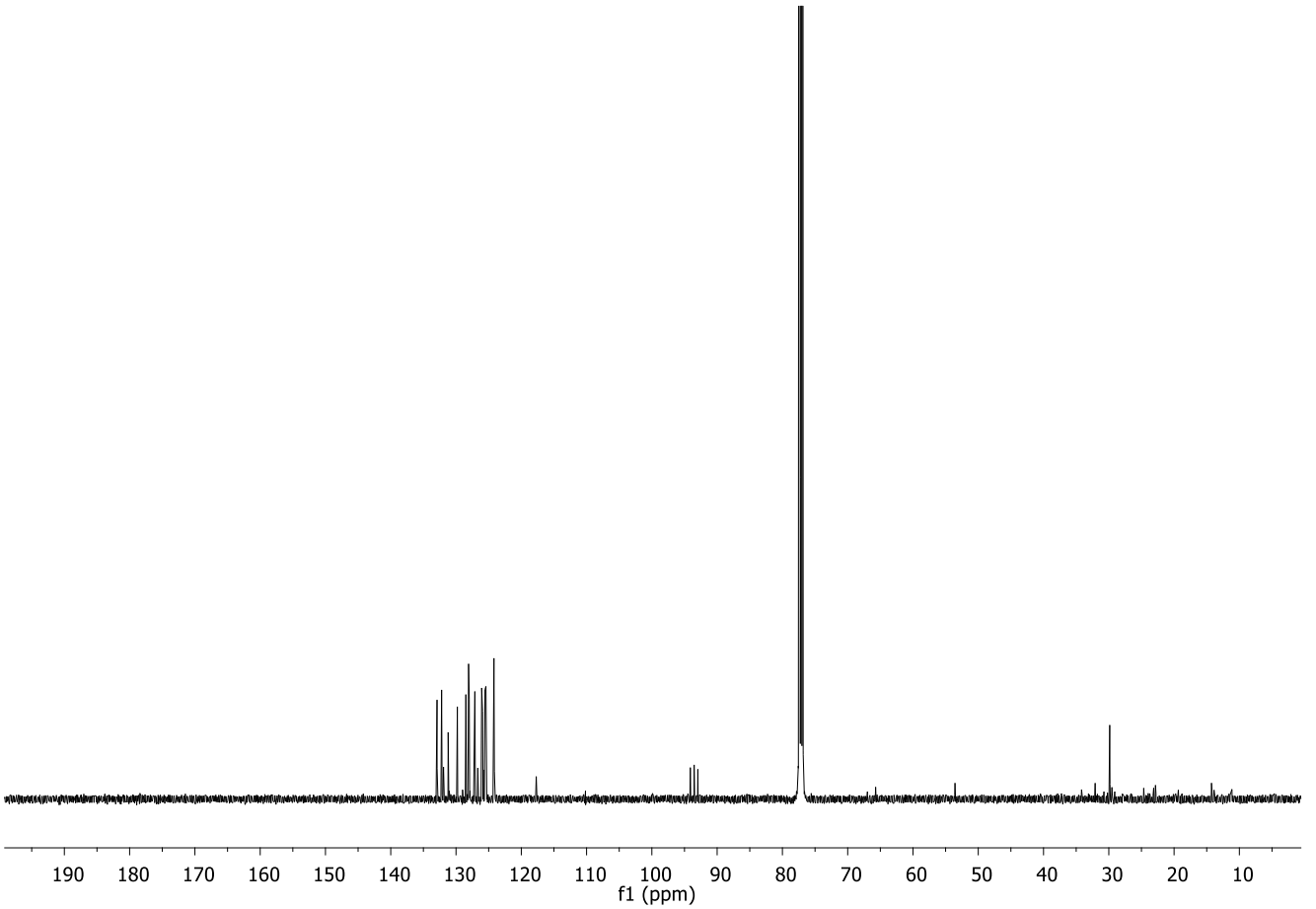


Compound 13



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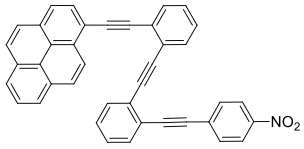
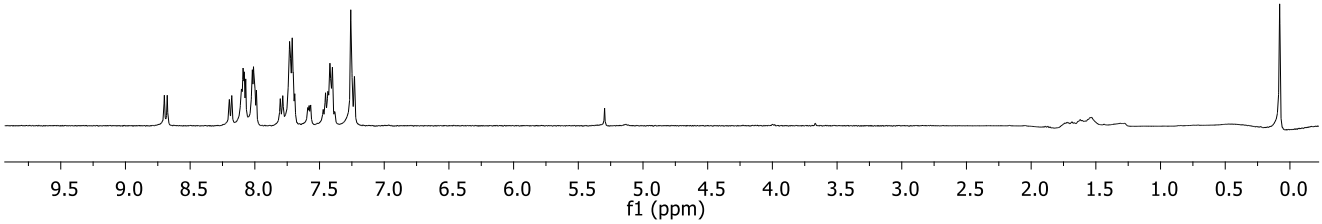
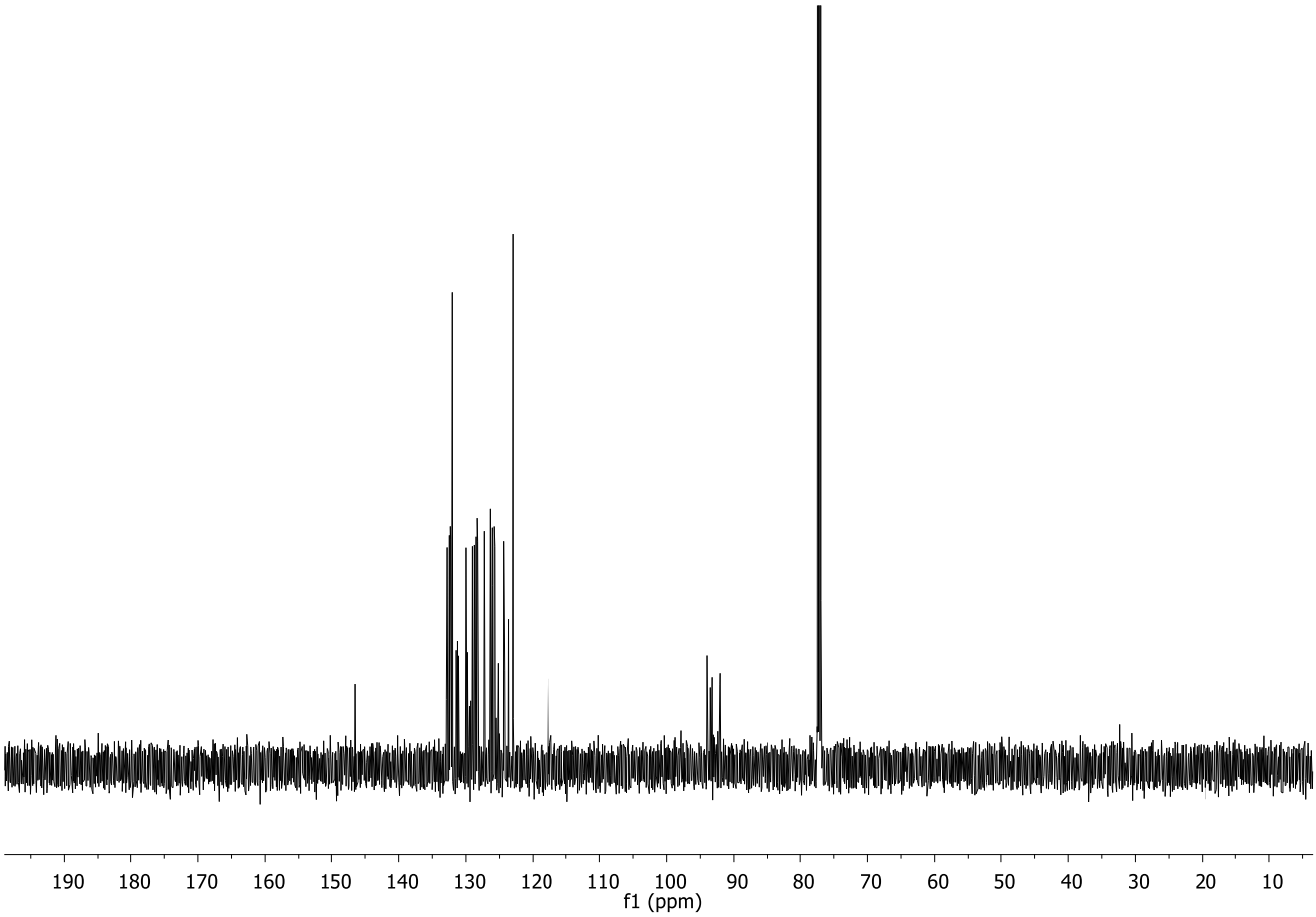



Compound 14



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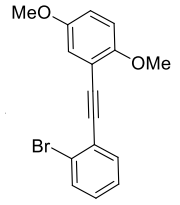
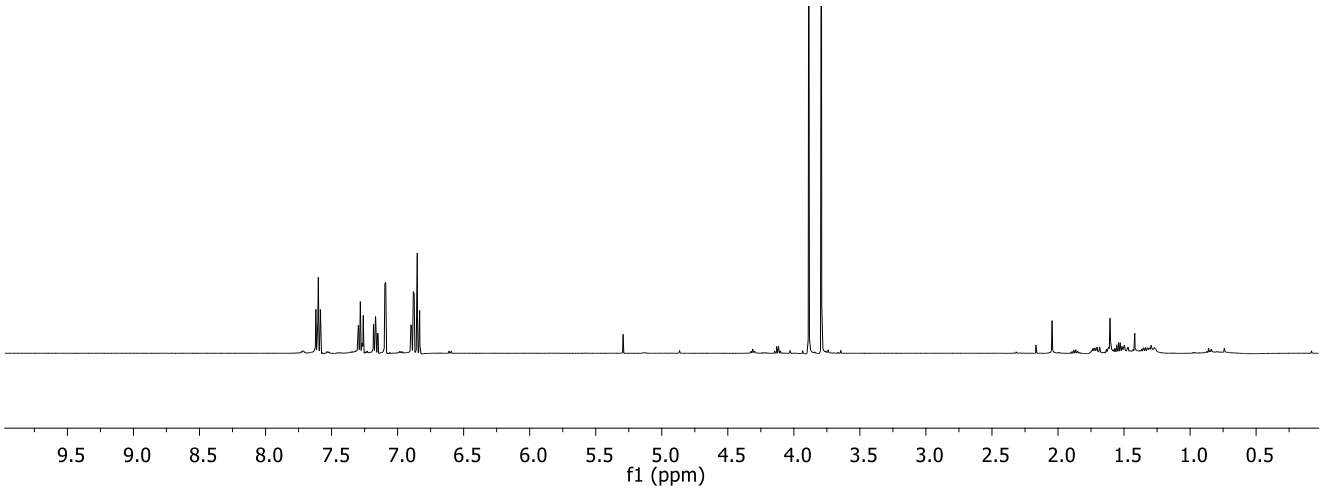
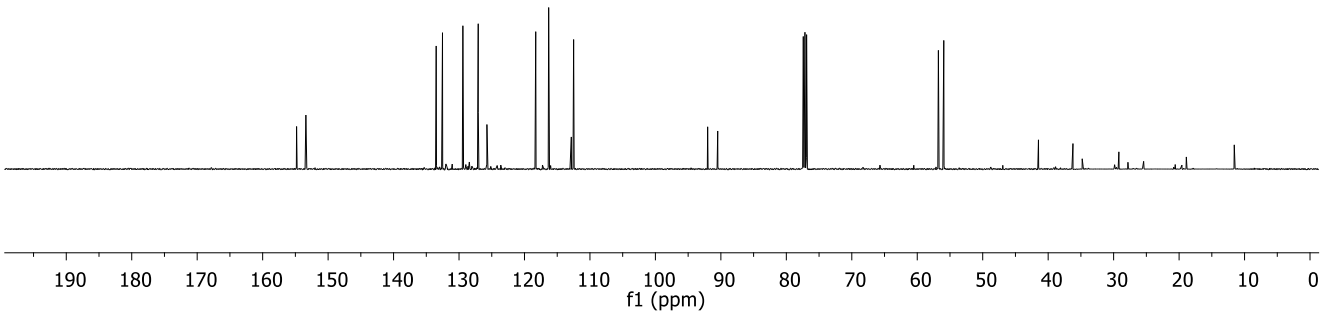



**VI**



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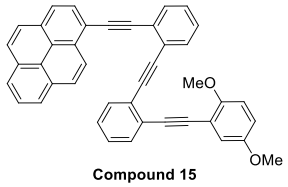
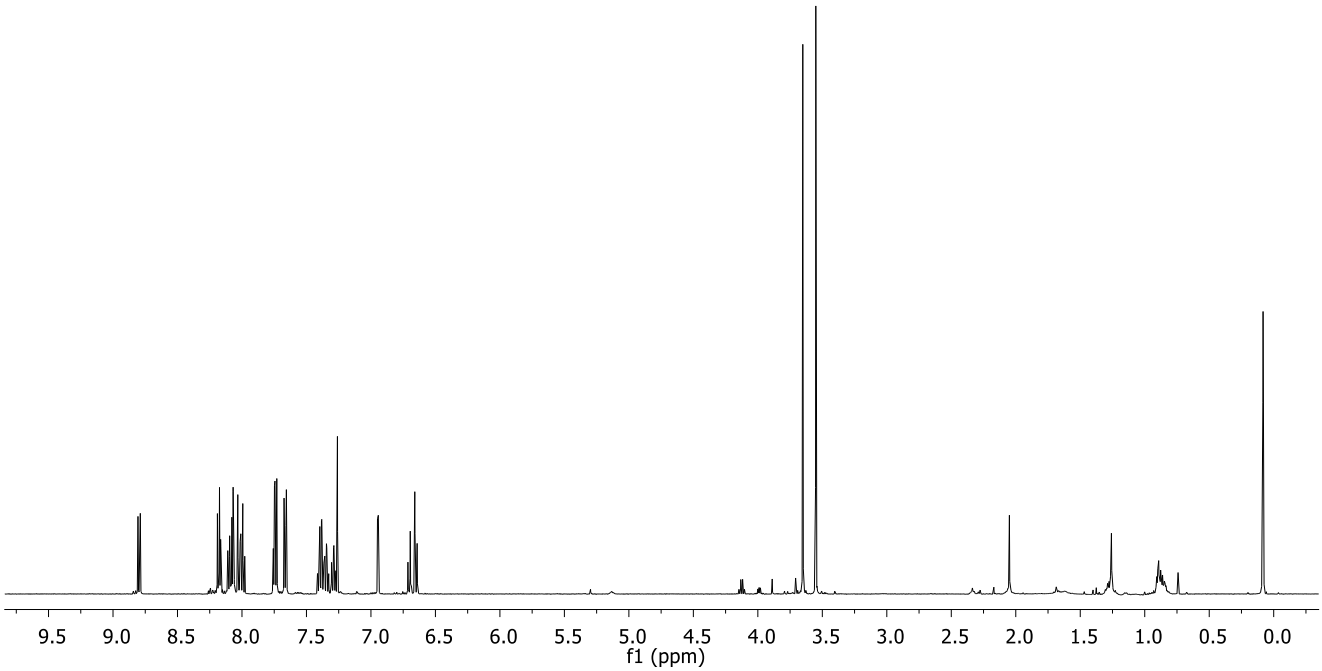
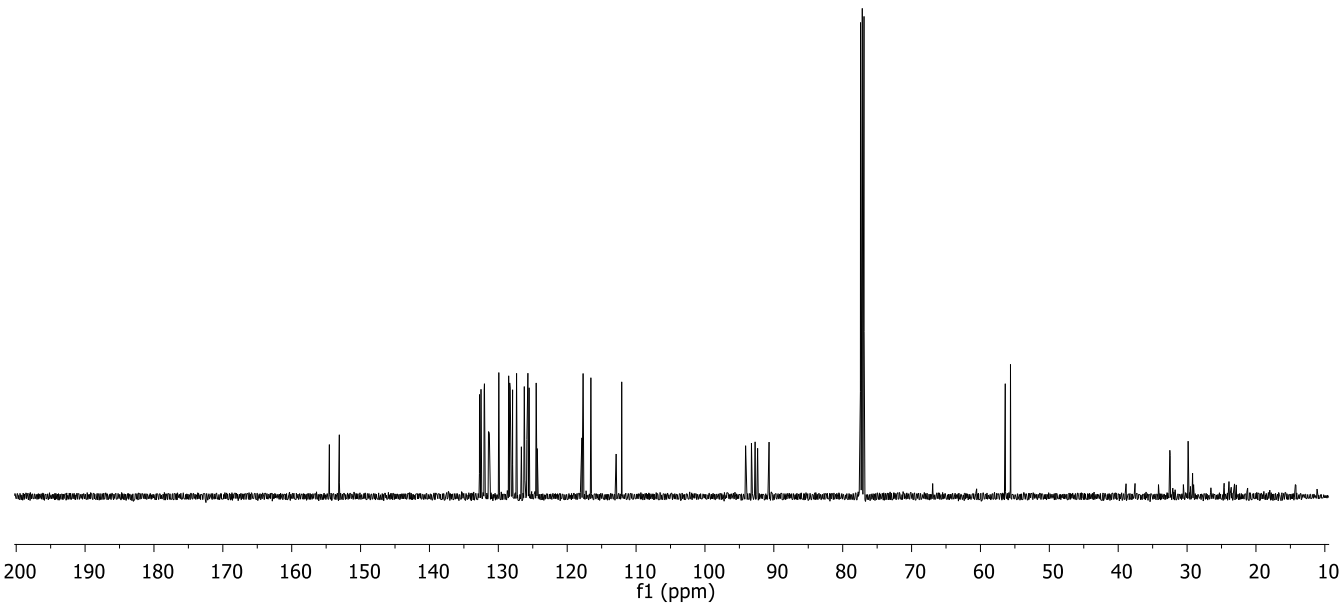



Compound 15



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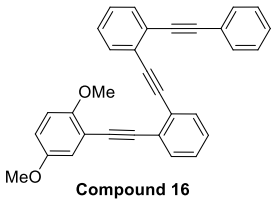


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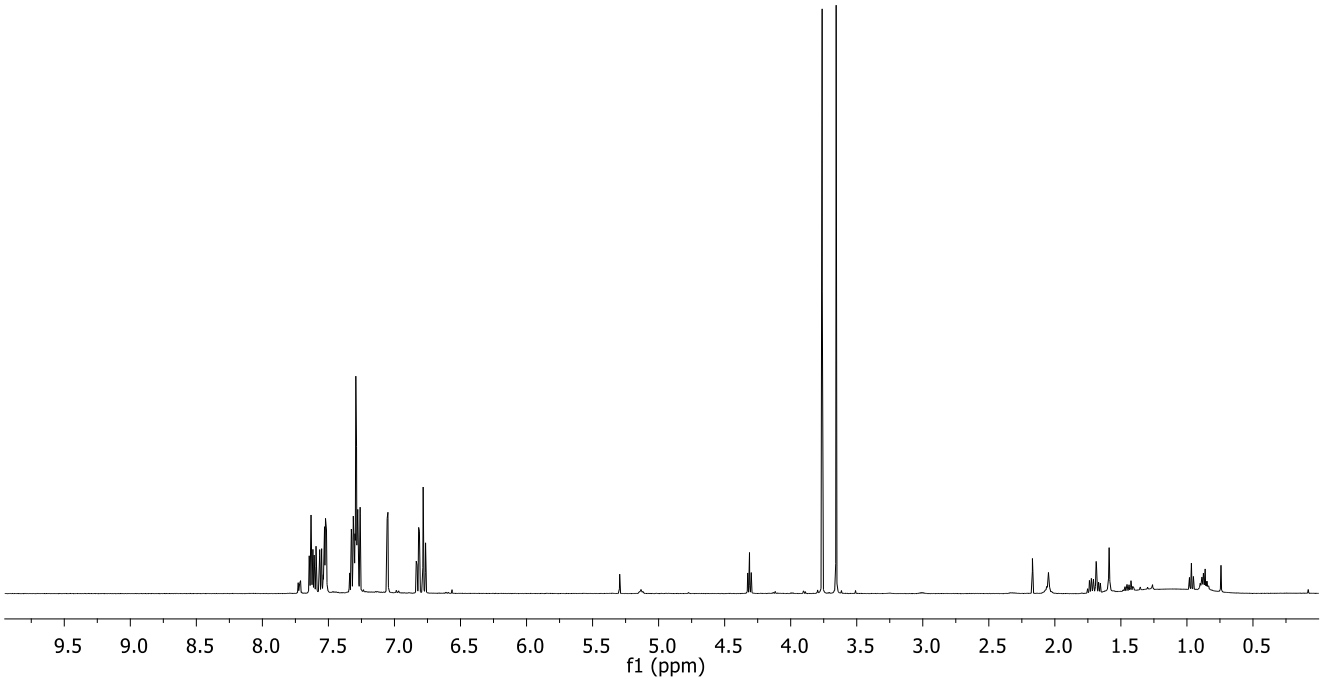
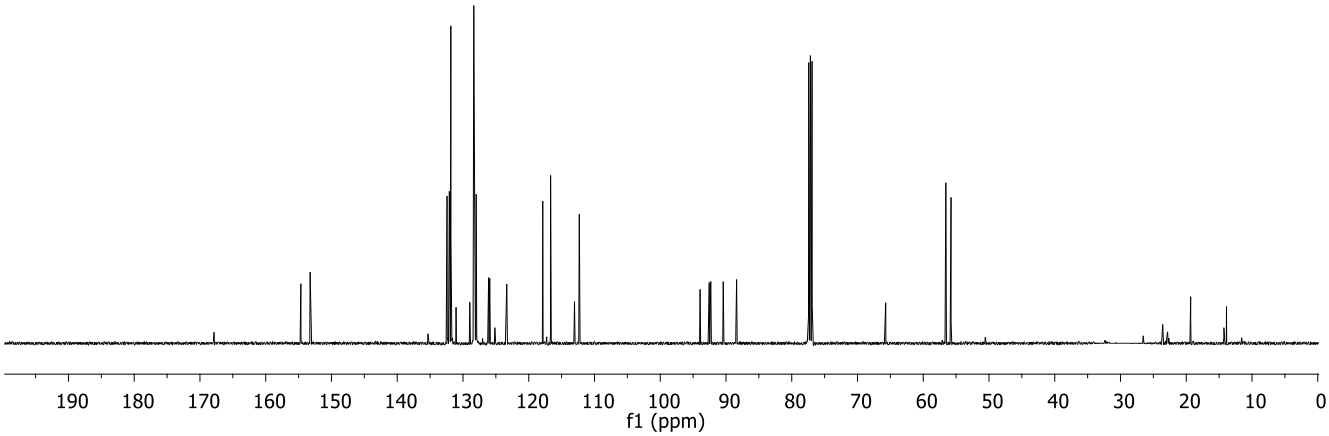
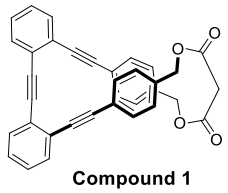


## Complex 1·Ag(I):



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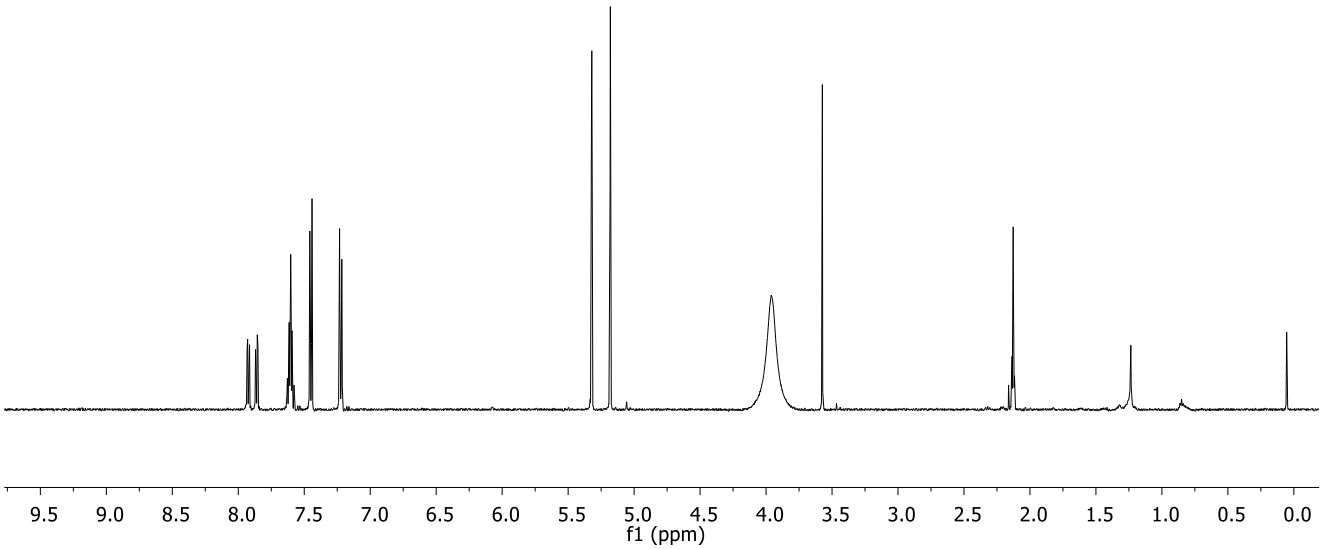


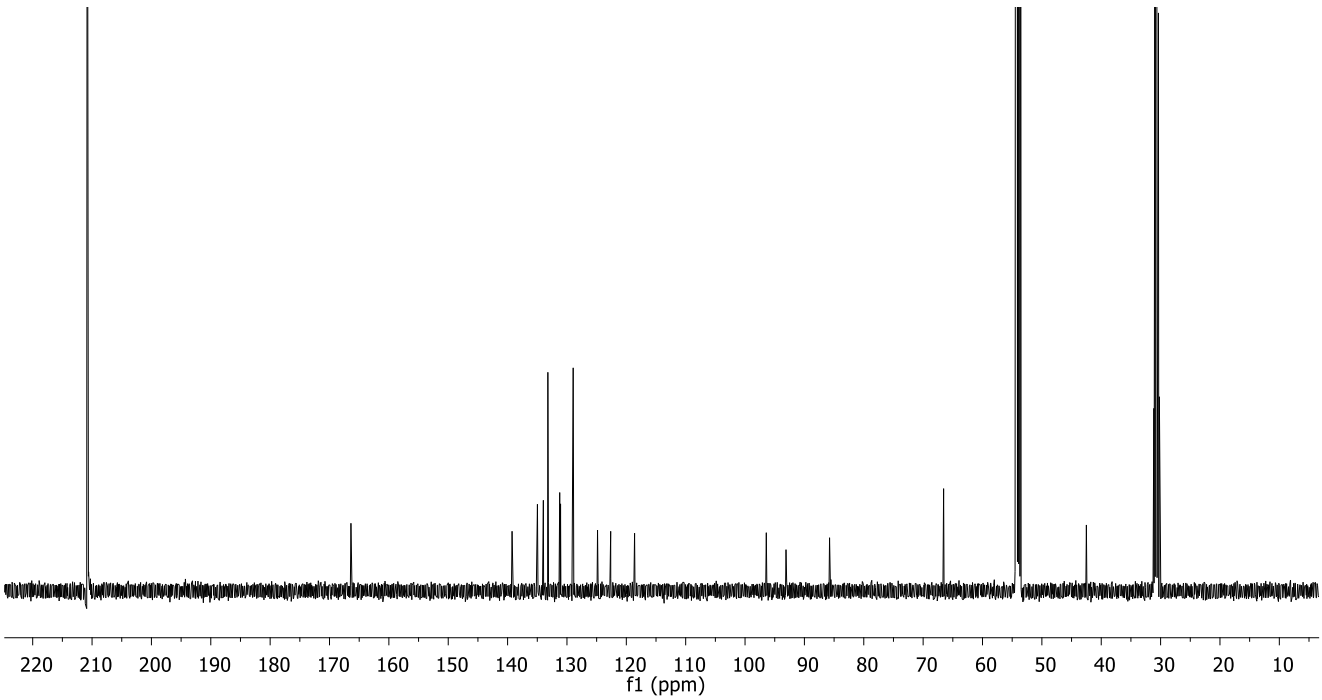

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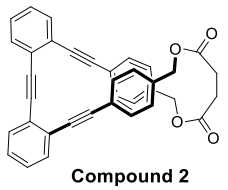
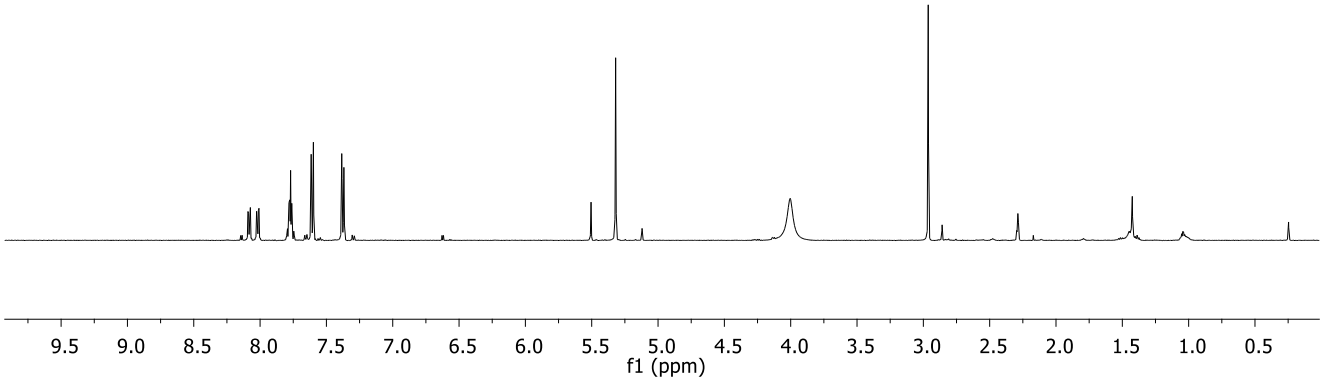
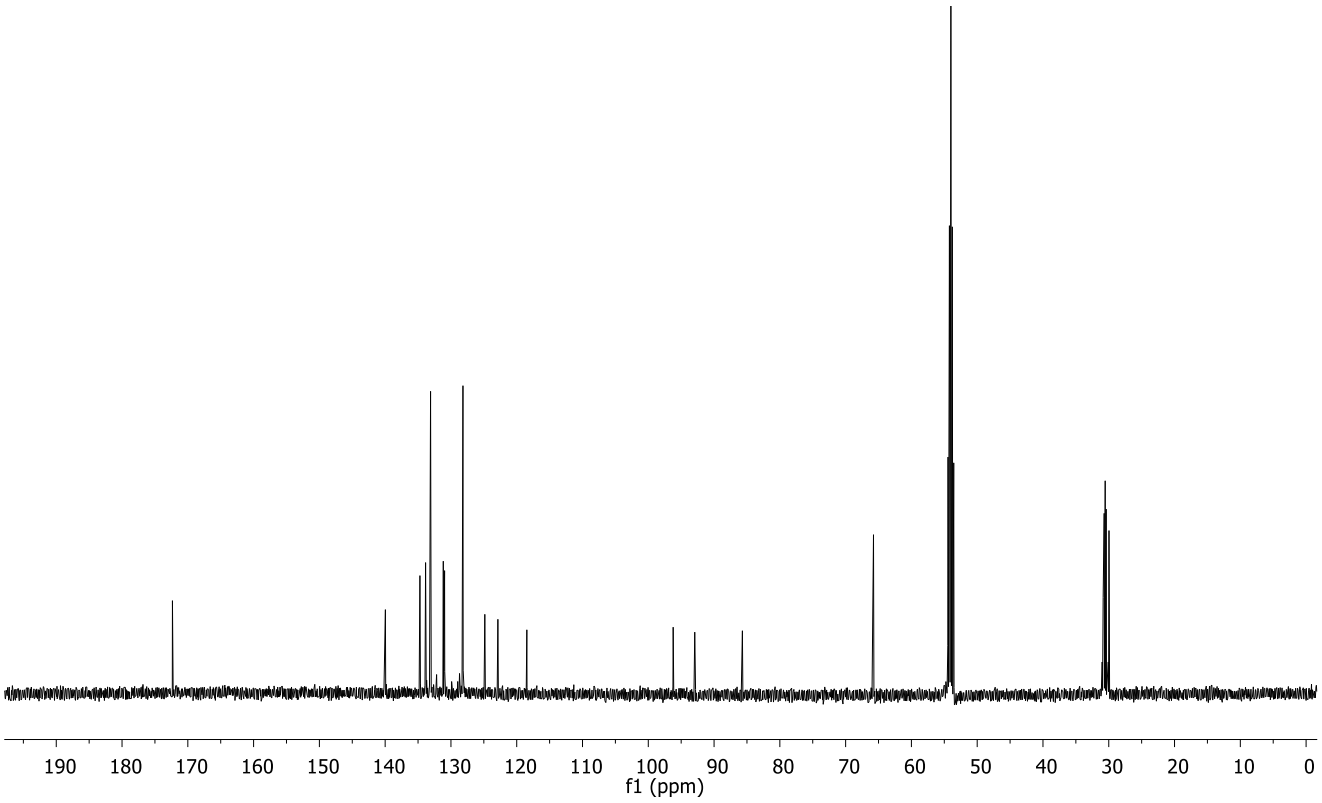


Compound 2



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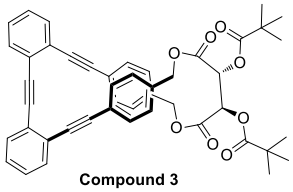
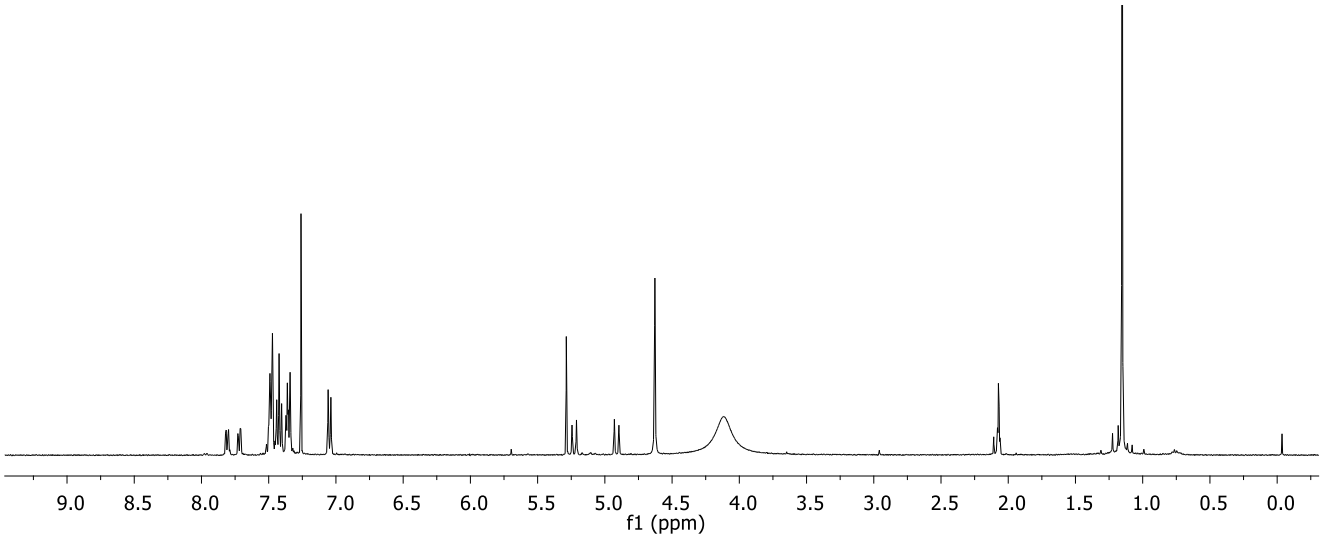


Compound 3

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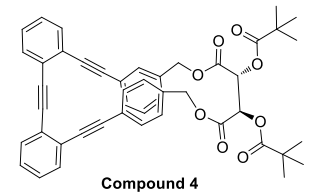
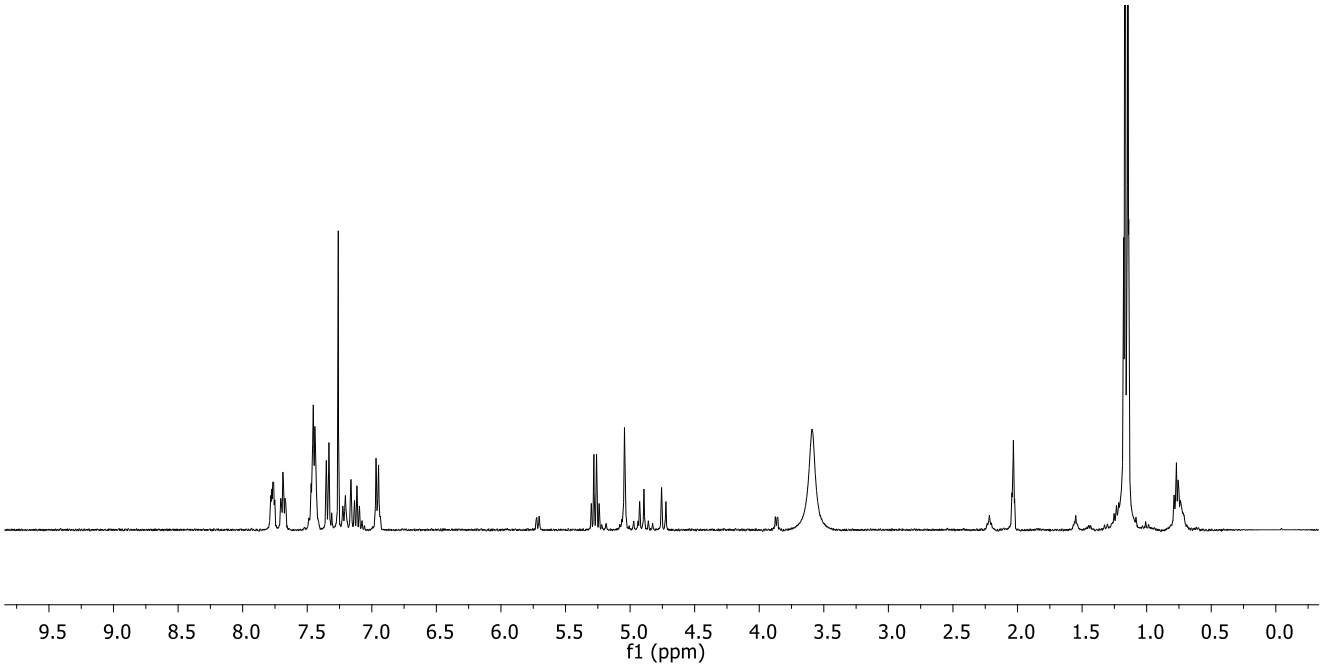


Compound 4



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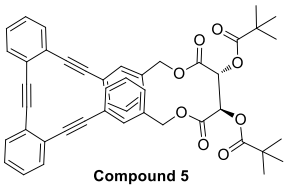
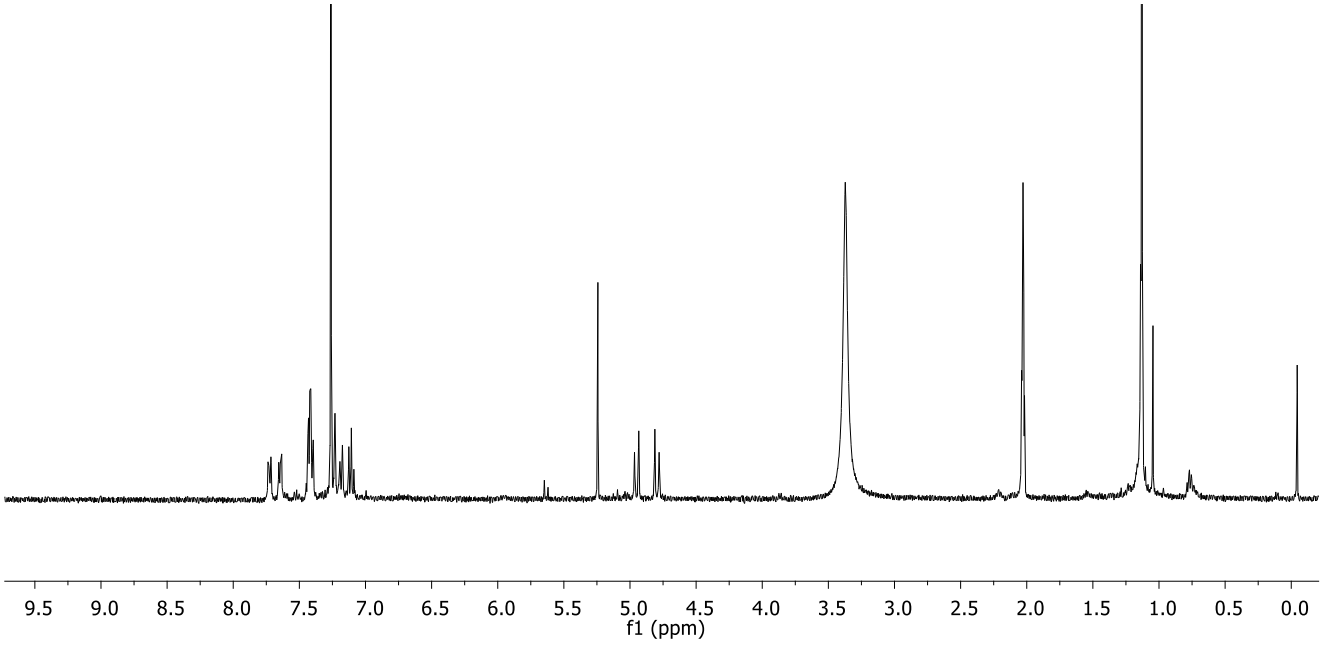


Compound 5



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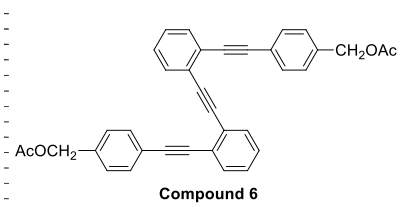


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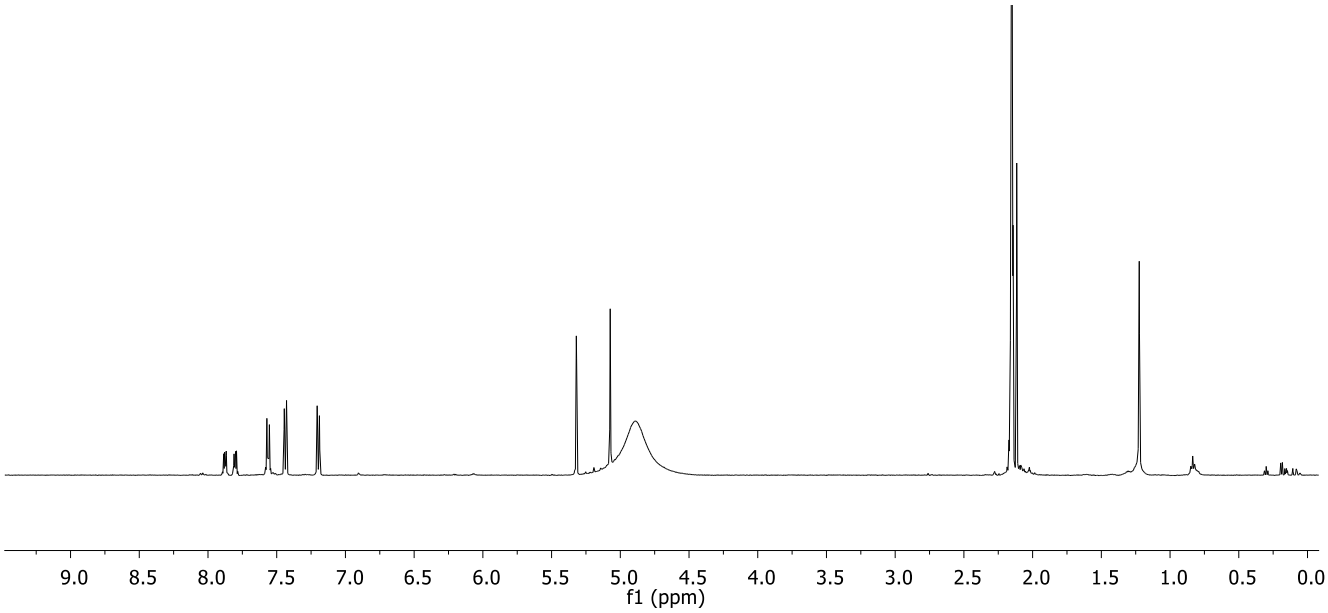

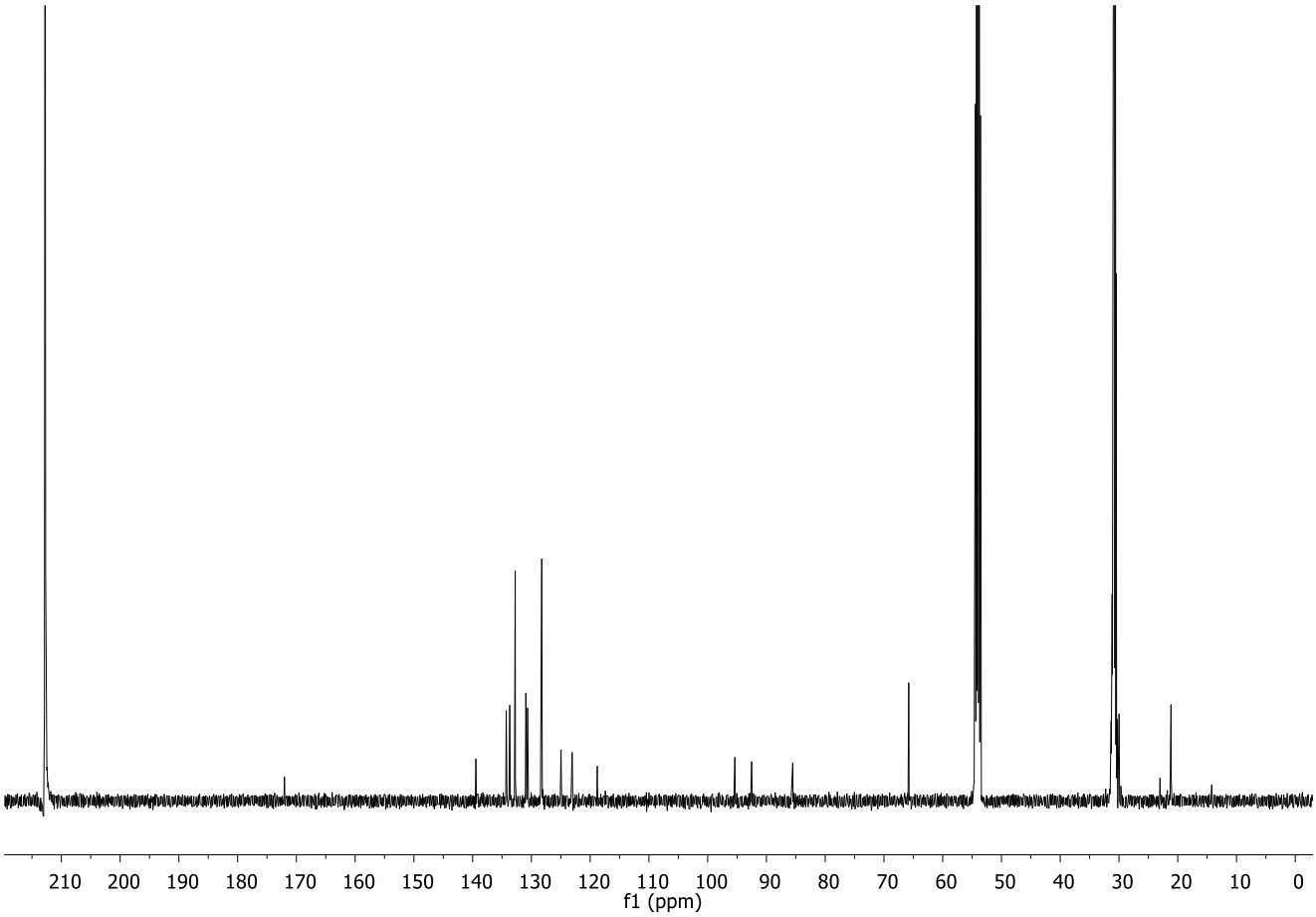
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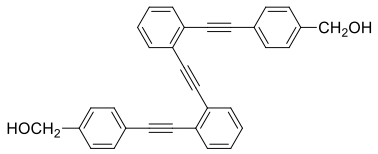
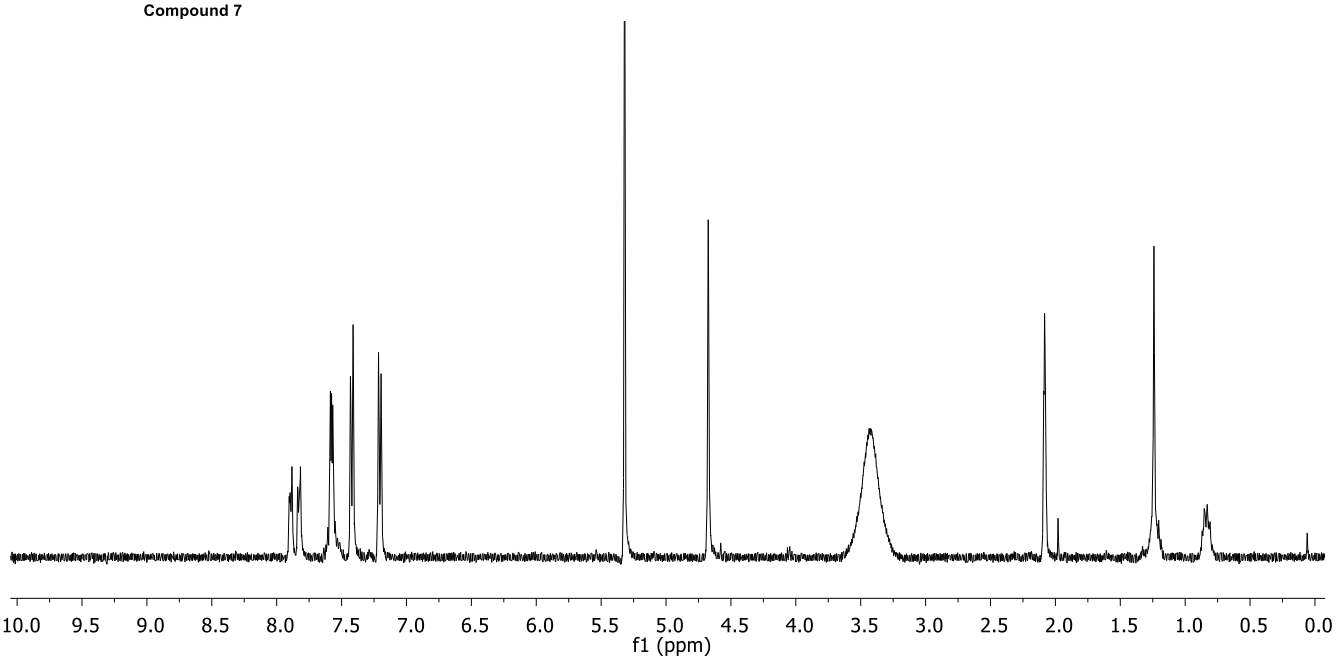
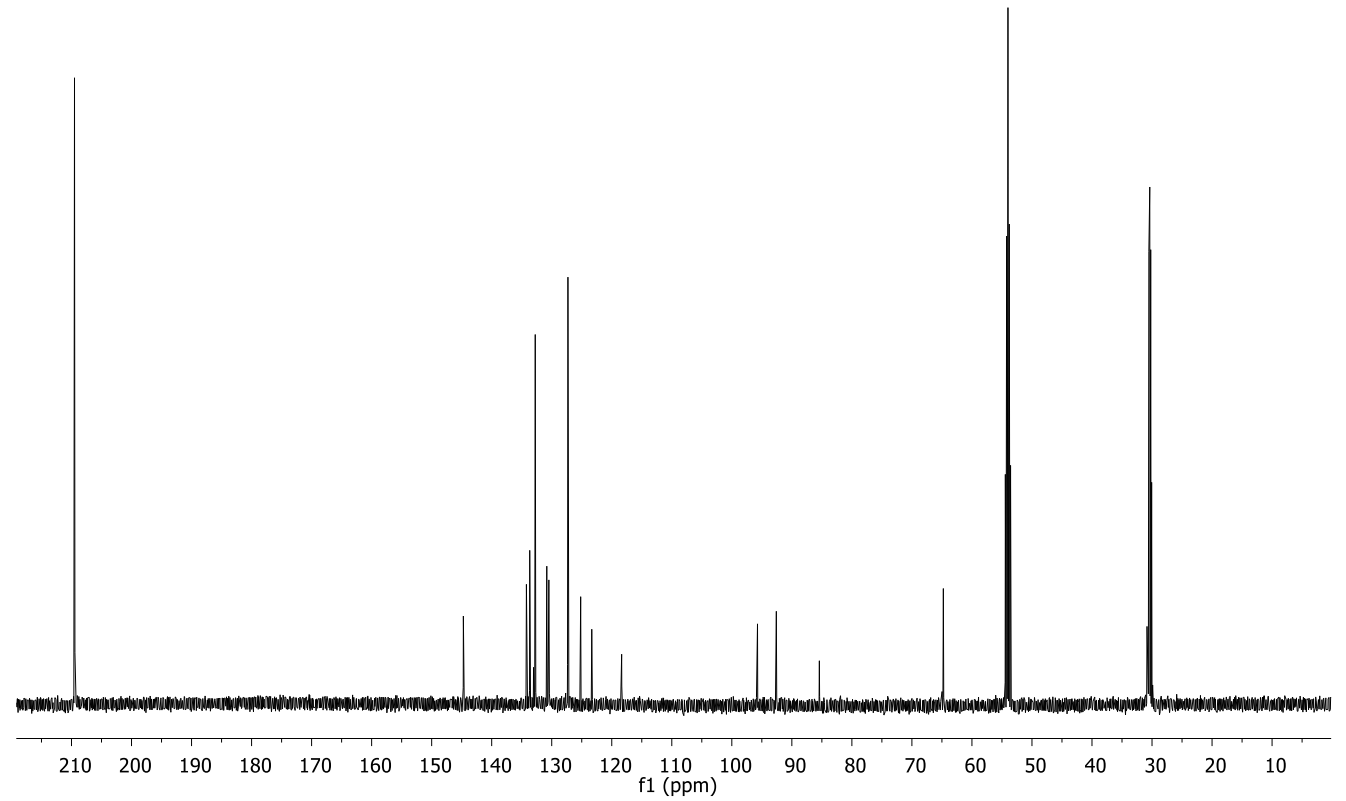



Compound 7

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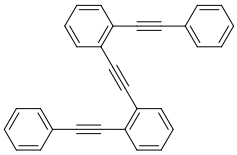
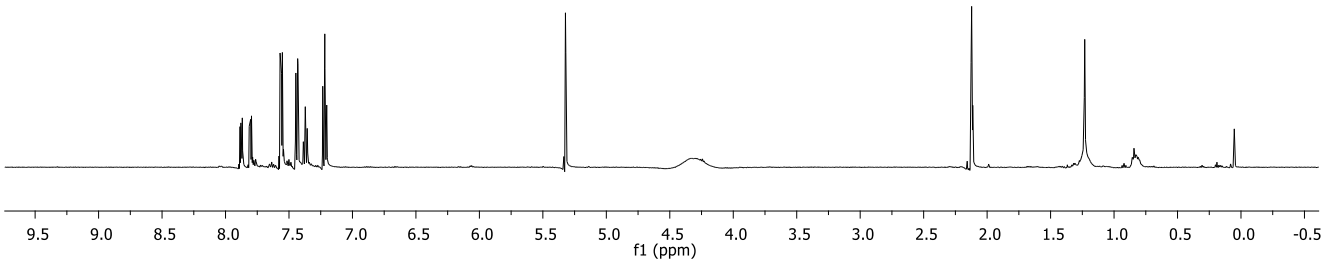
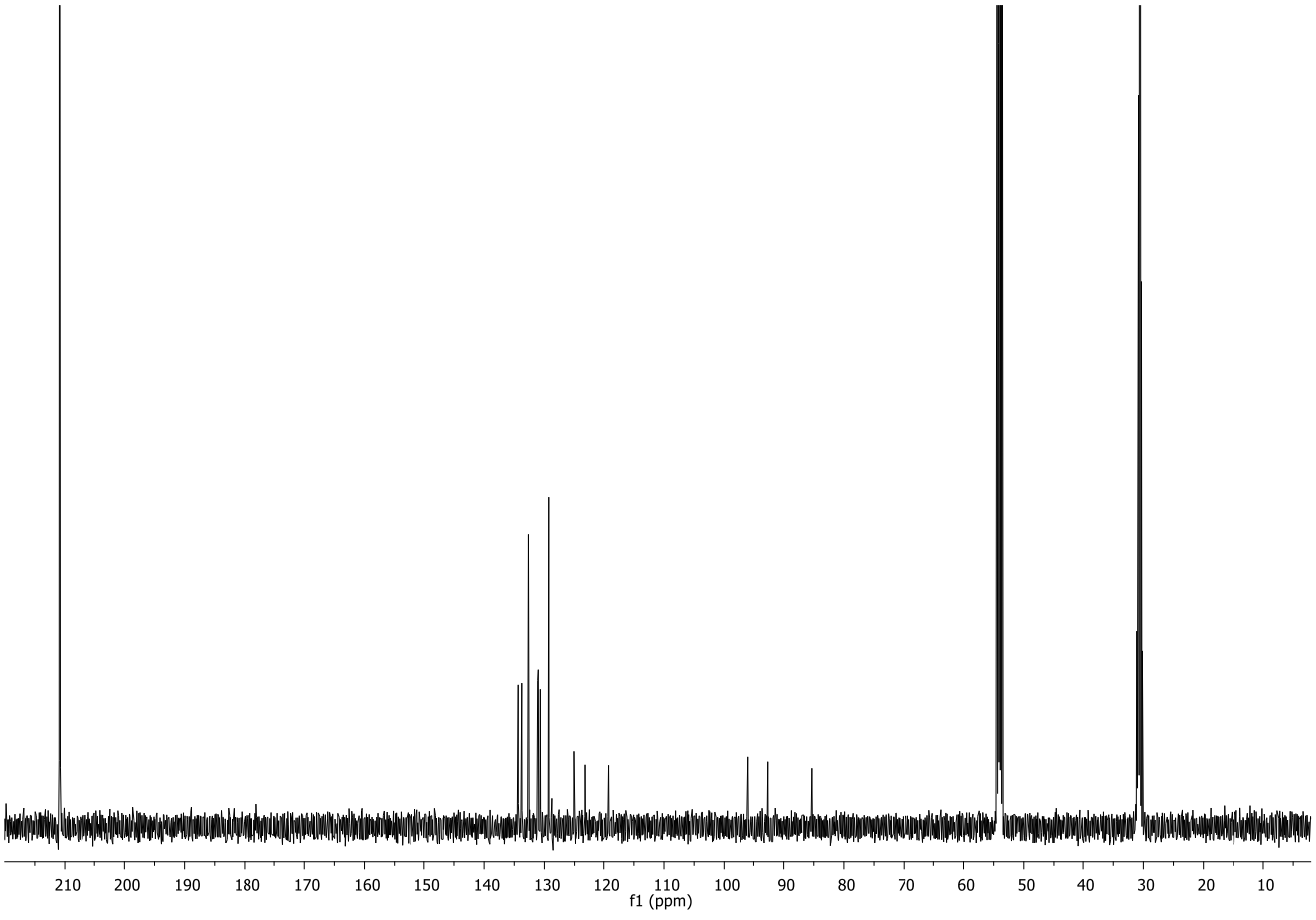


Compound 8



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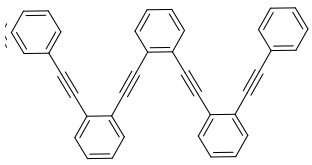
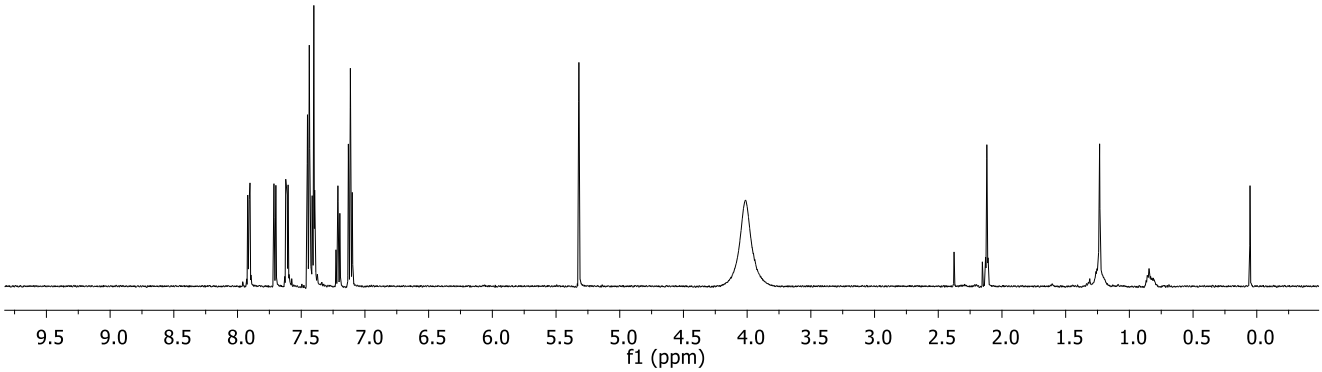
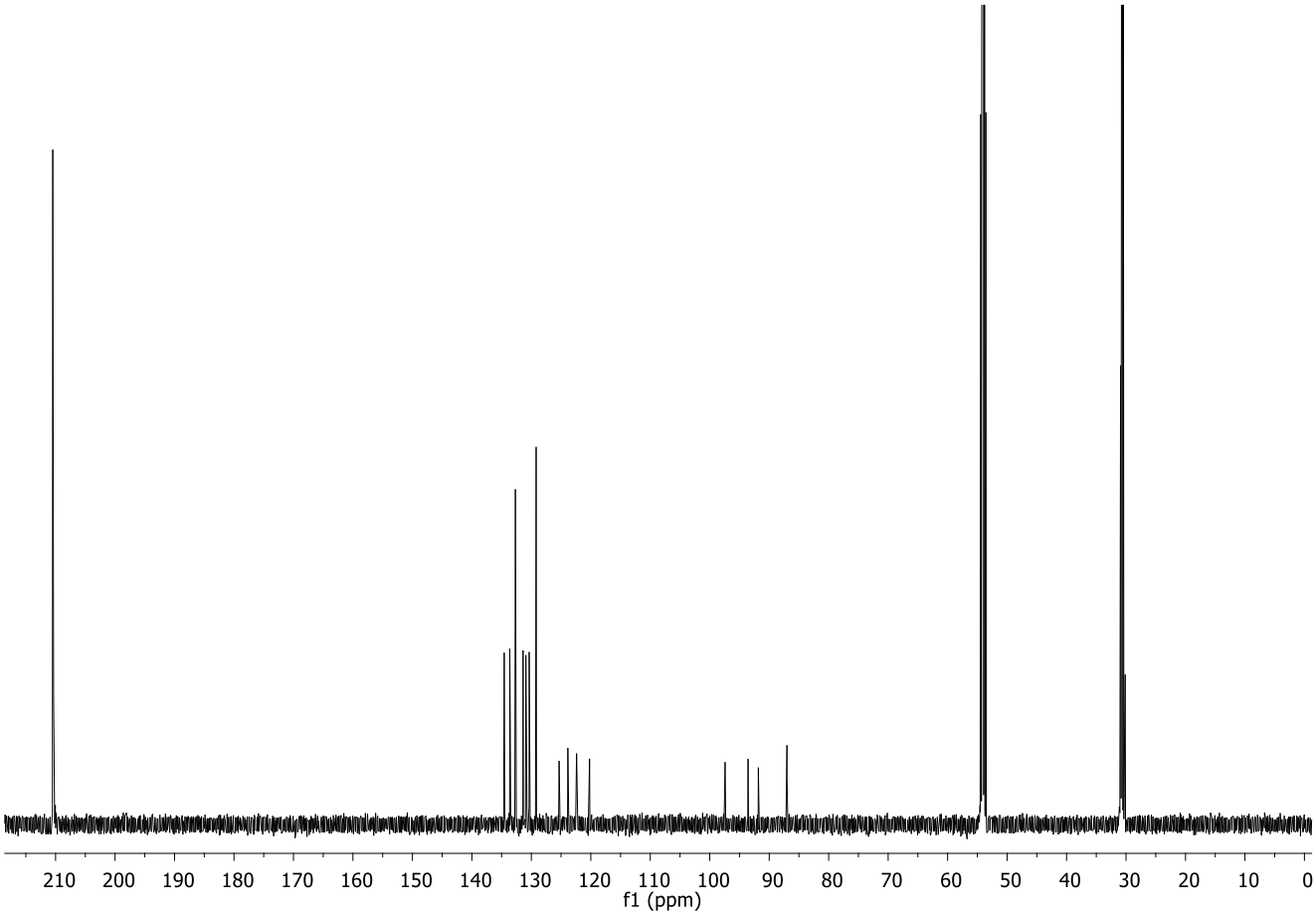
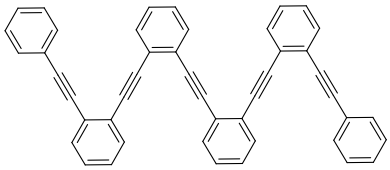


Compound 9

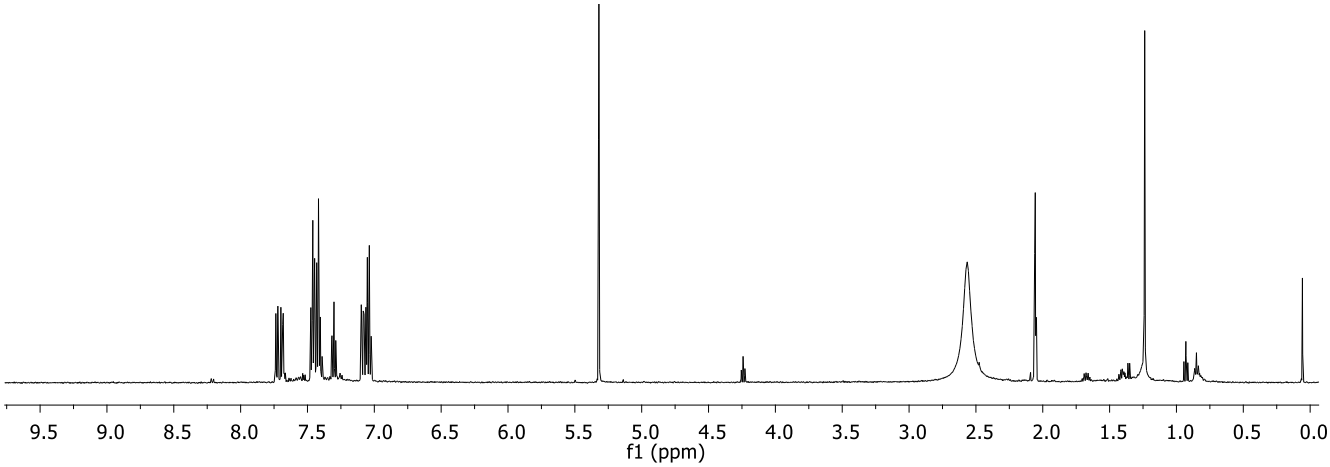


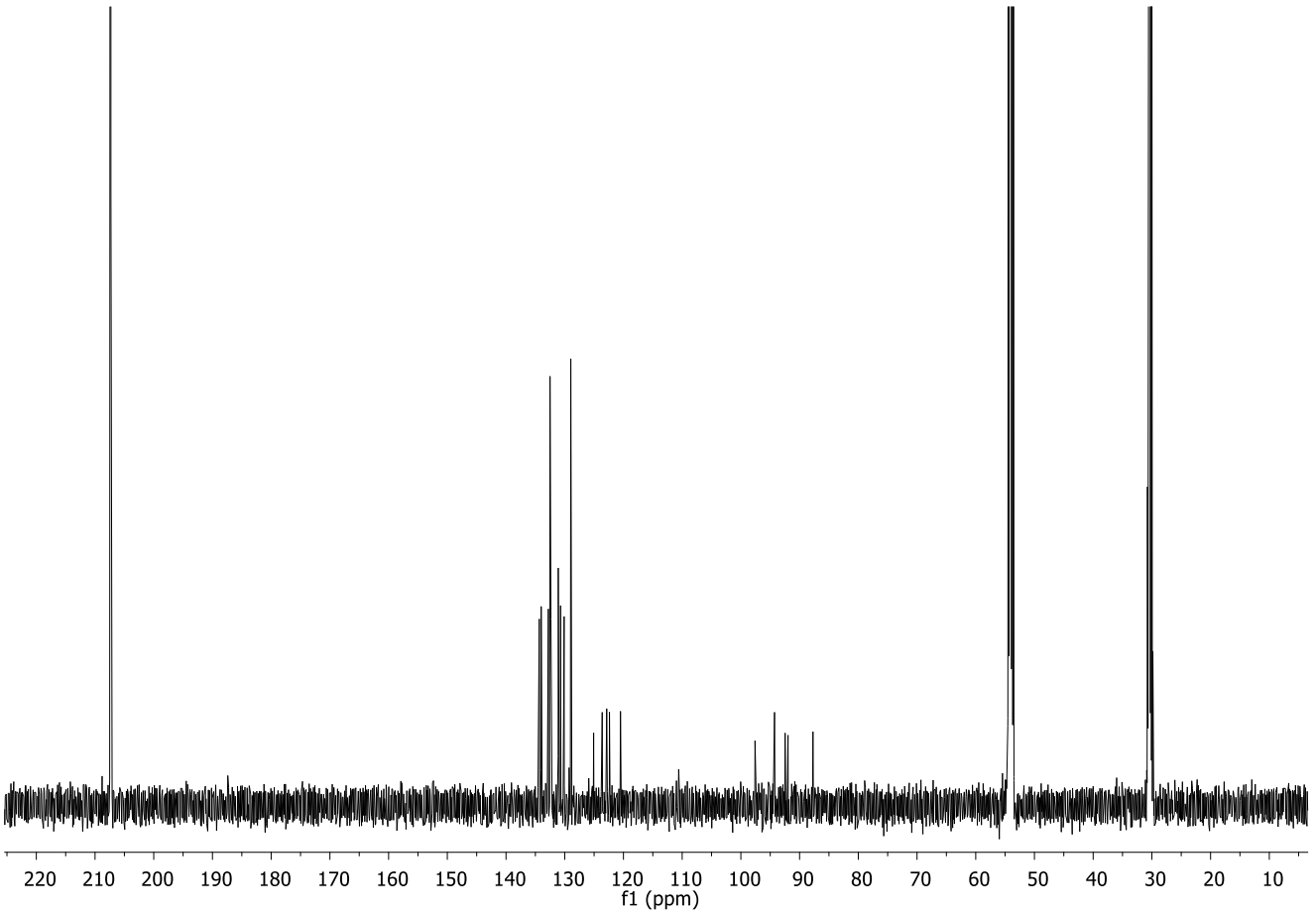



## Complex 10·Ag(I):

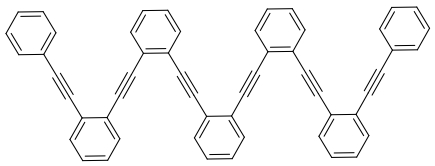


Compound 10

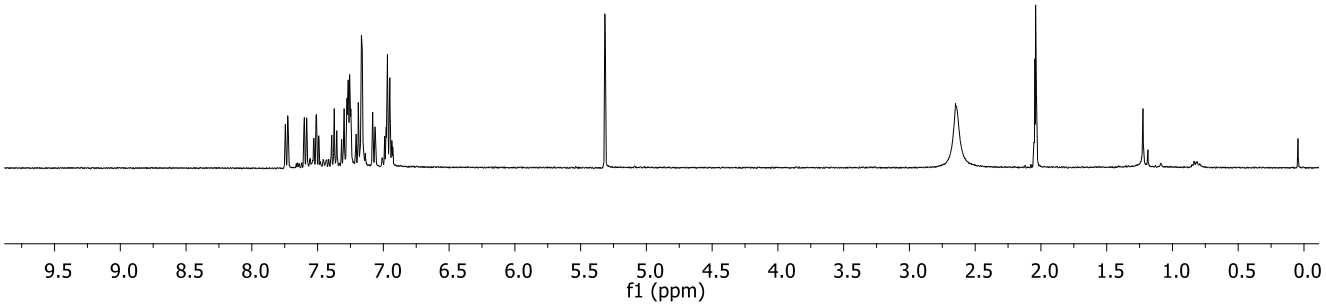


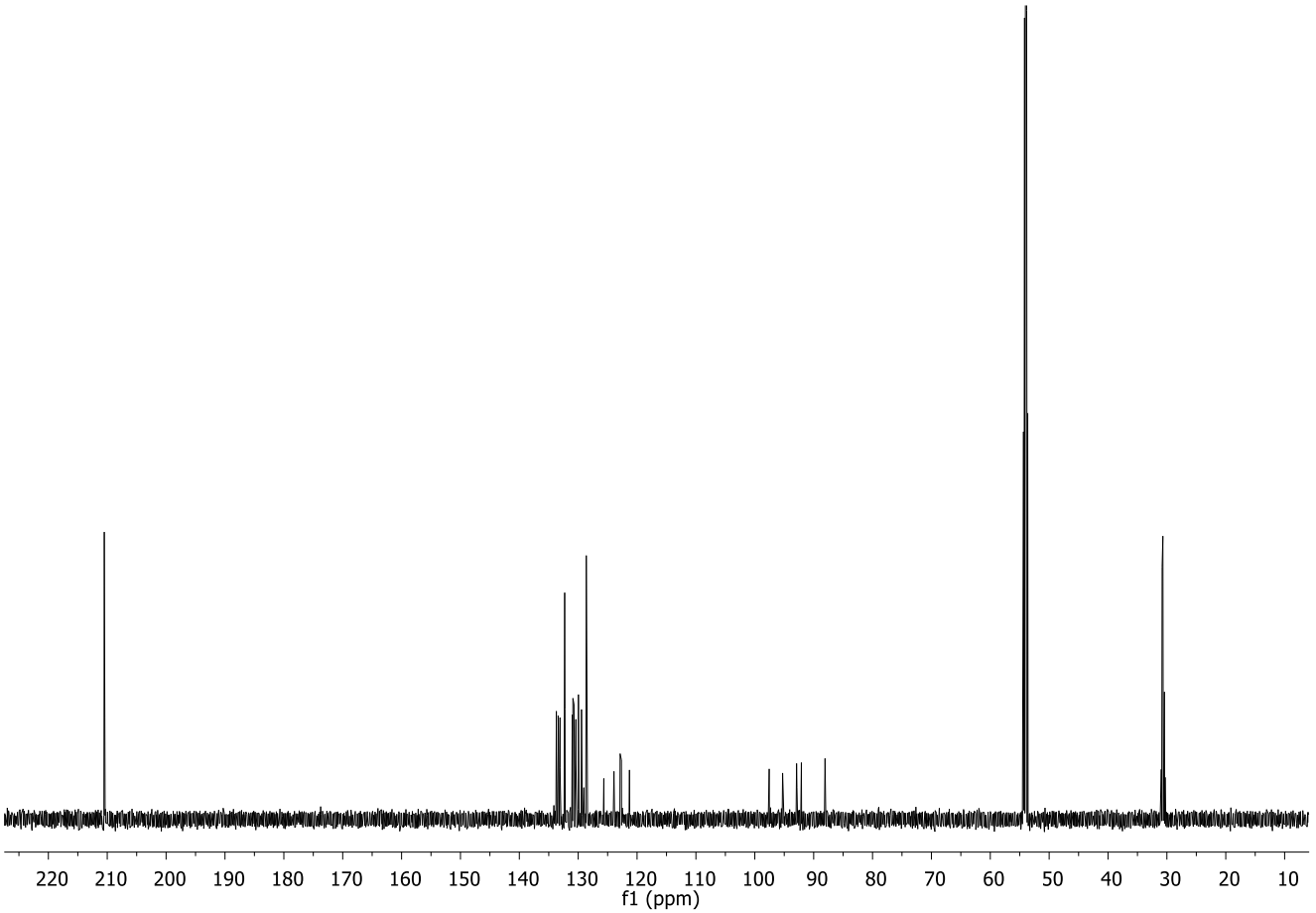



## Complex 11·Ag(I):



Compound 11



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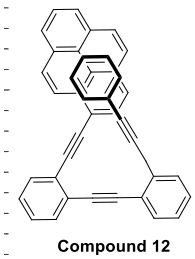
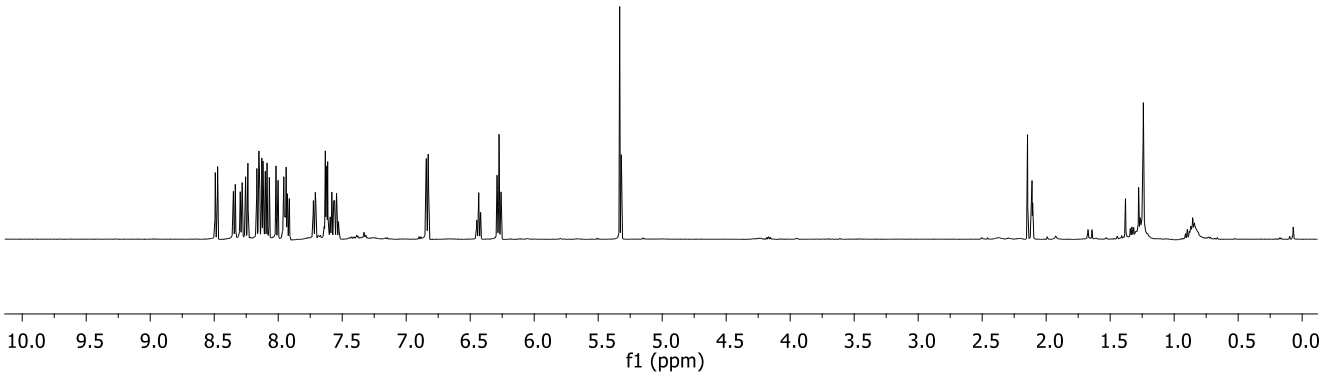
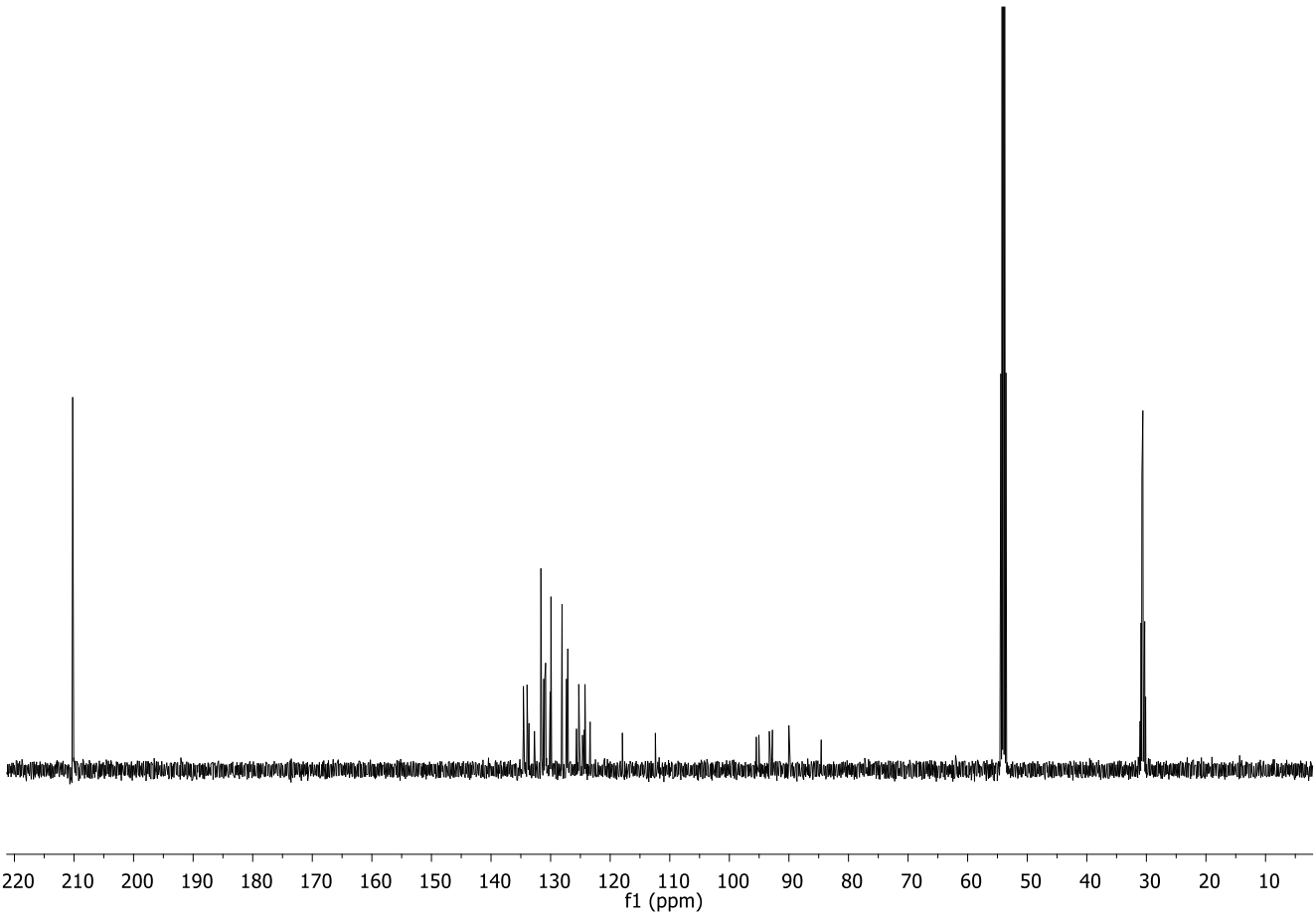
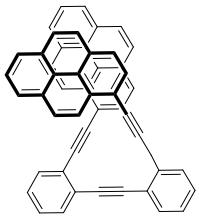


Compound 12

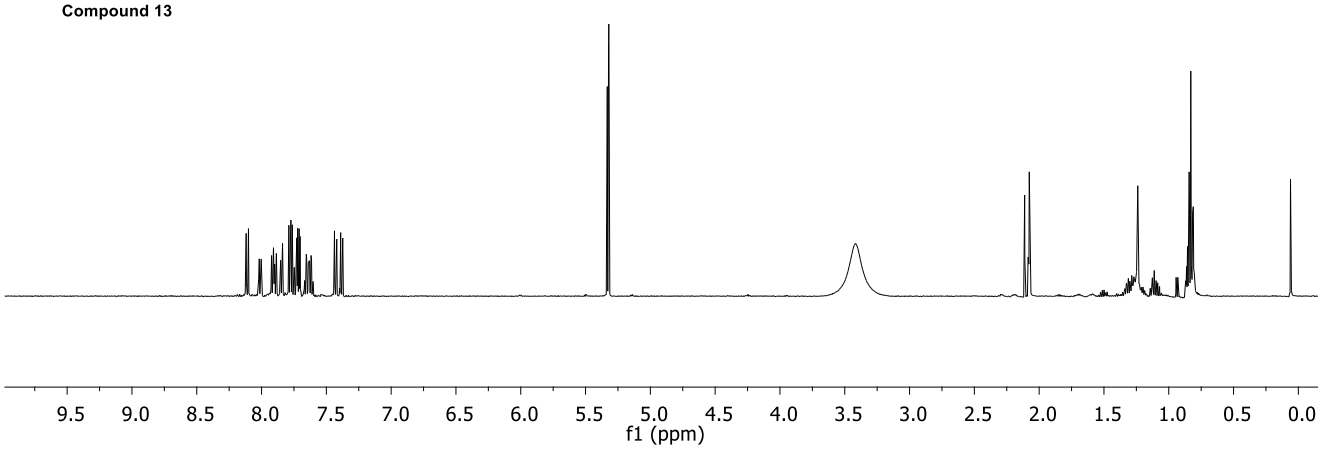


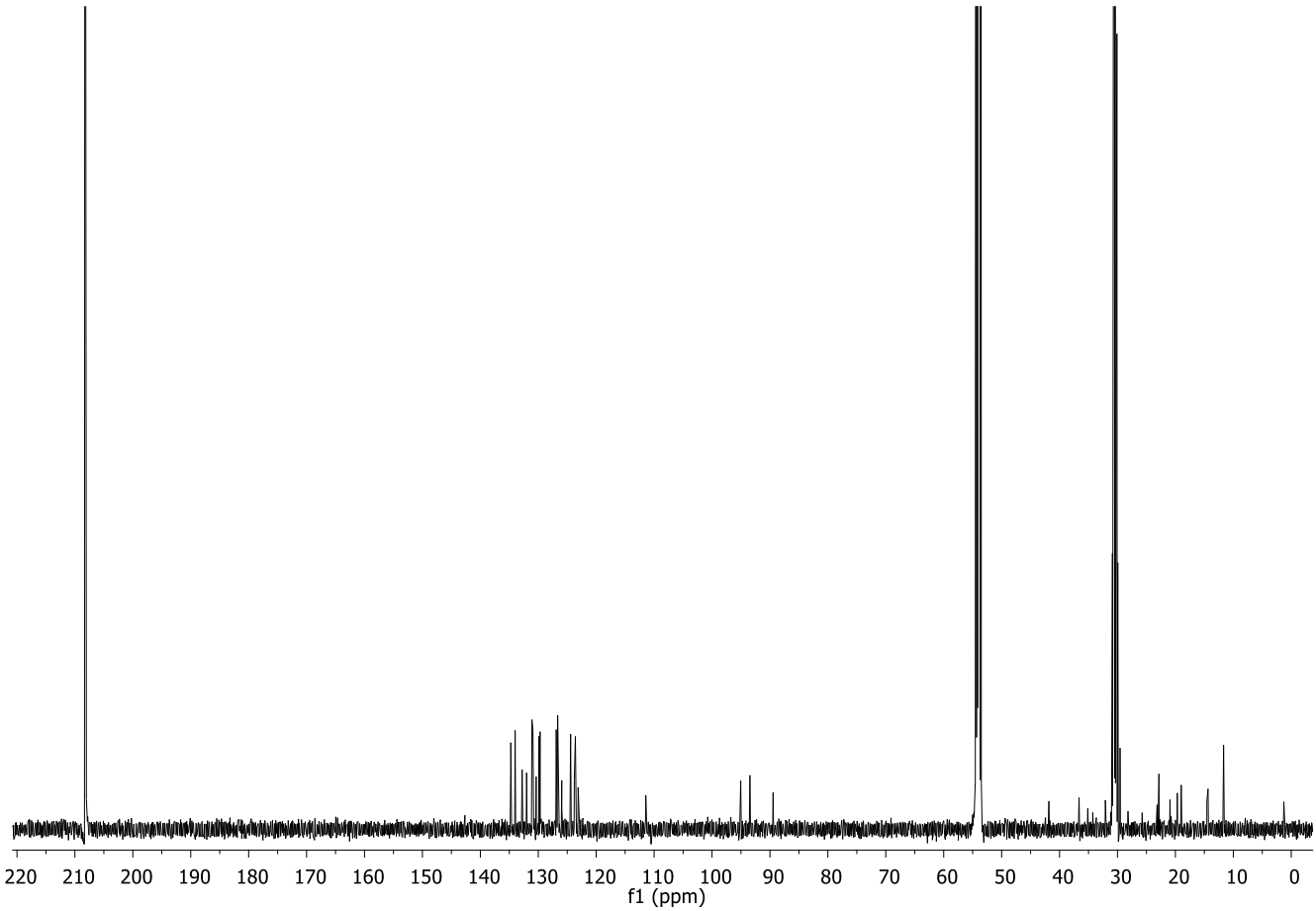



## Complex 13·Ag(I):

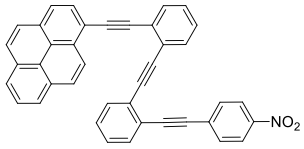


Compound 13

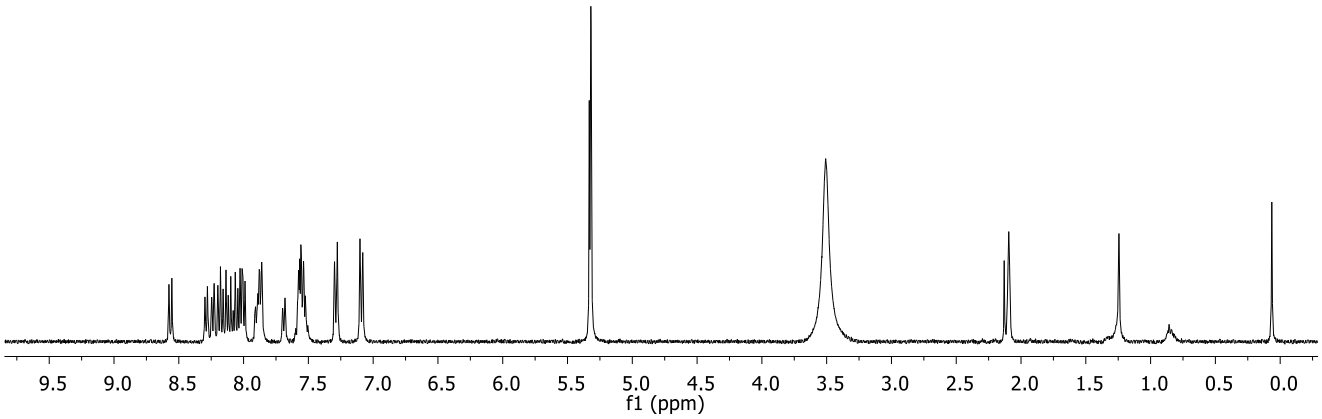


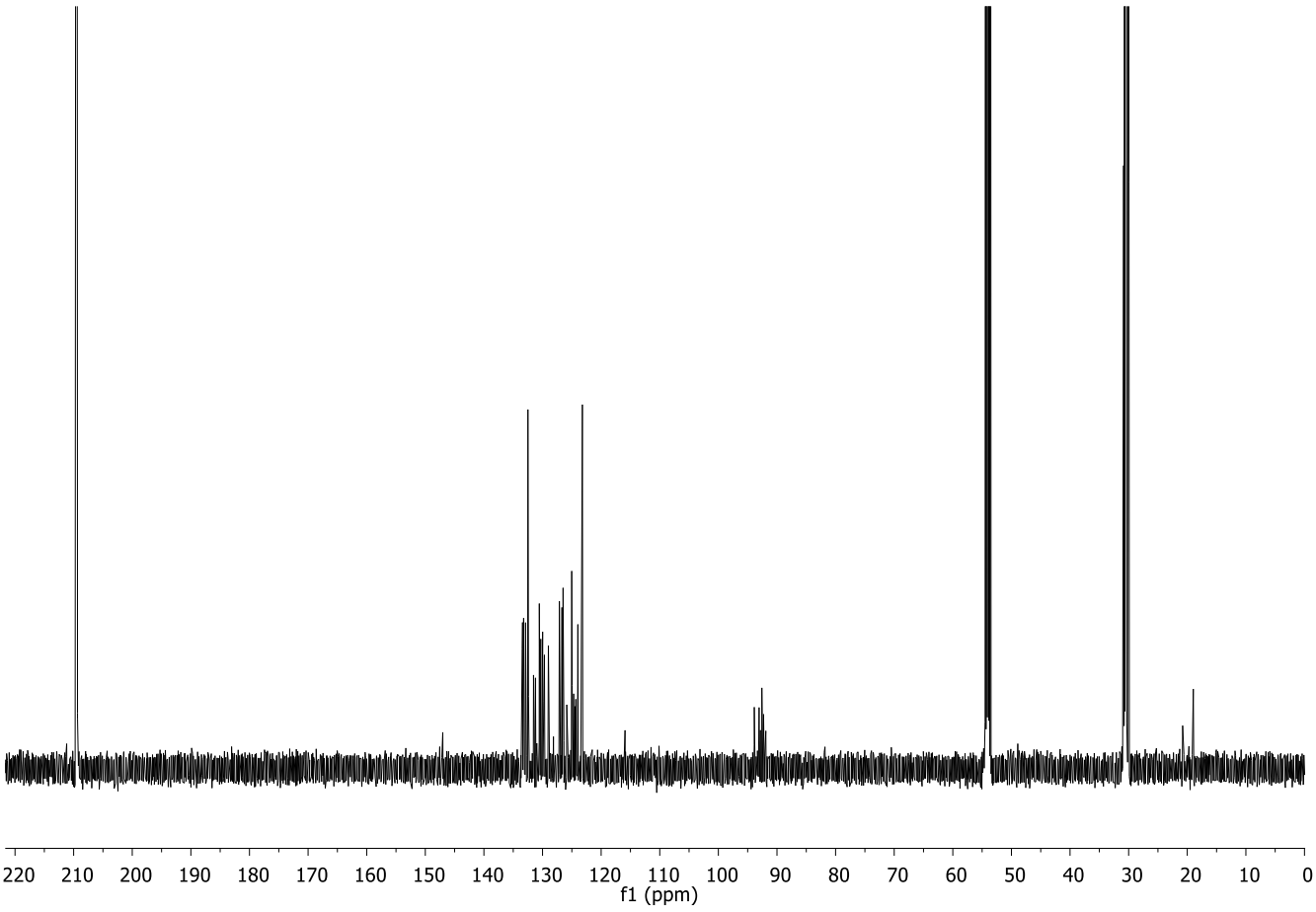



## Complex 14·Ag(I):

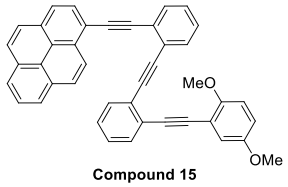



Compound 14

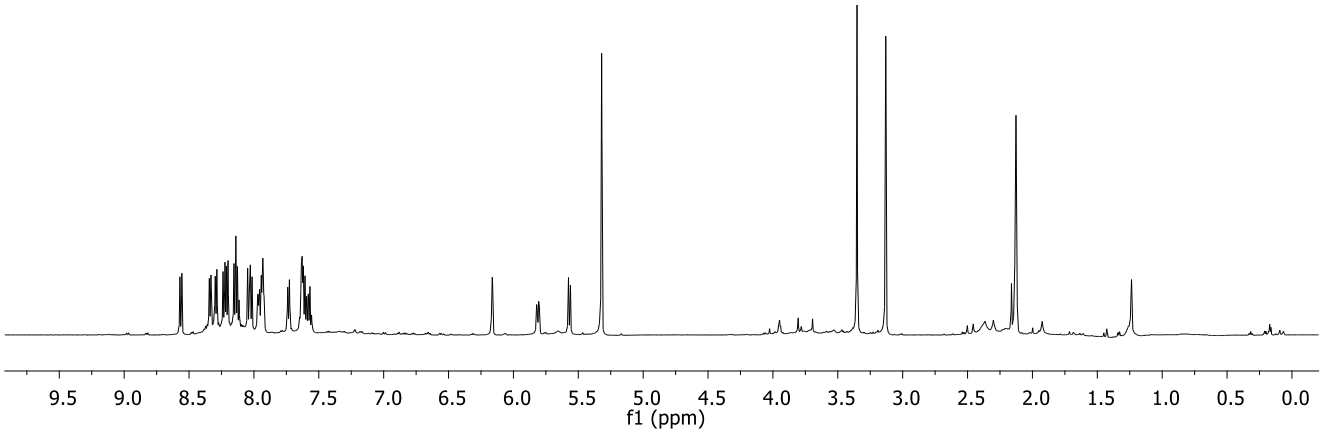


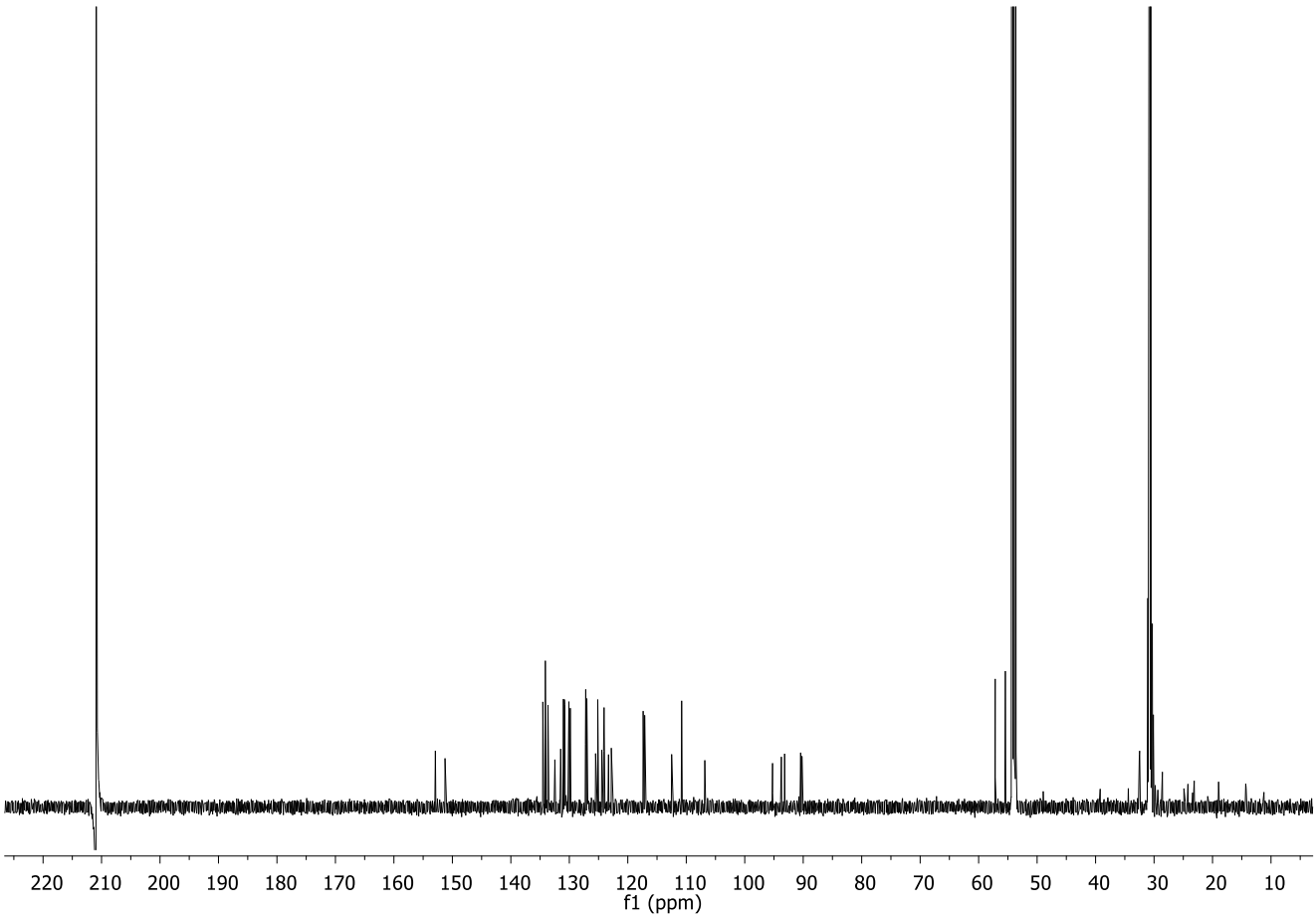



## Complex 15·Ag(I):

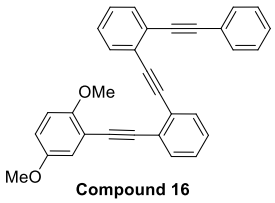



Compound 15

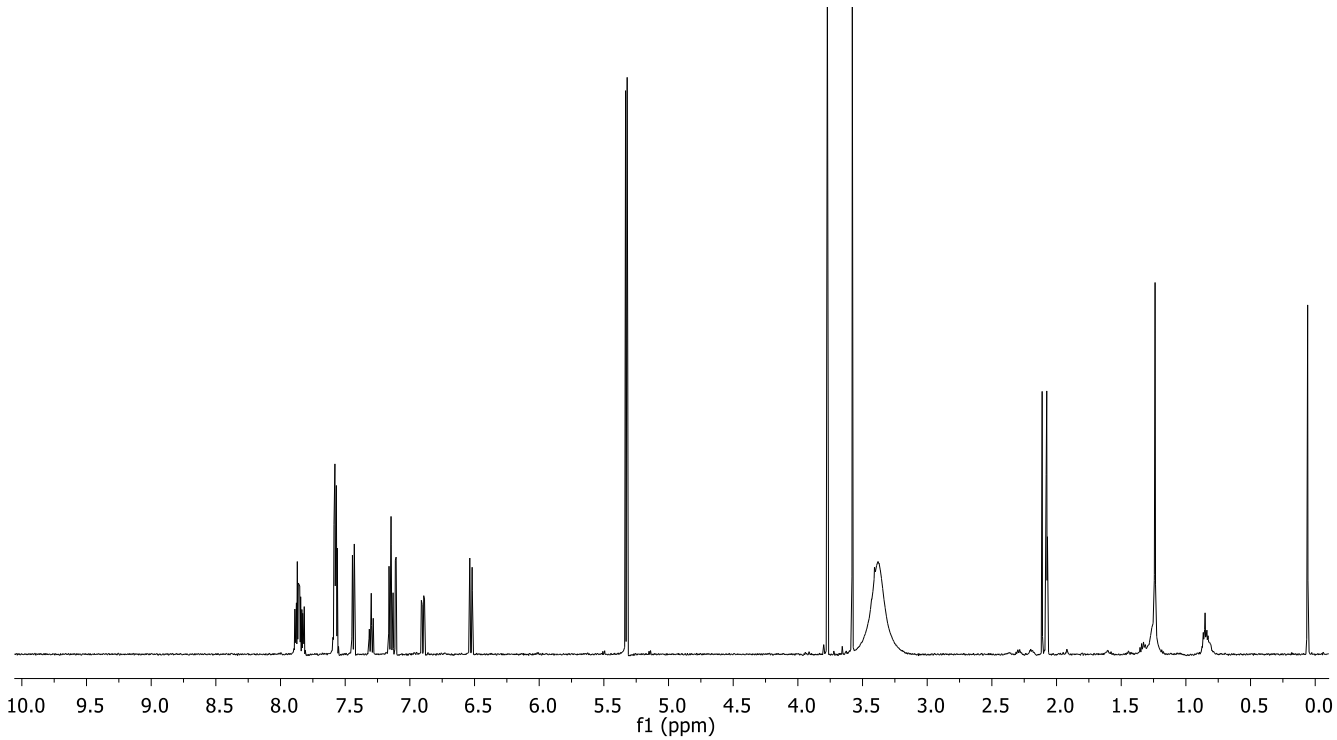


## Complex 16·Ag(I):




**Compound 16**



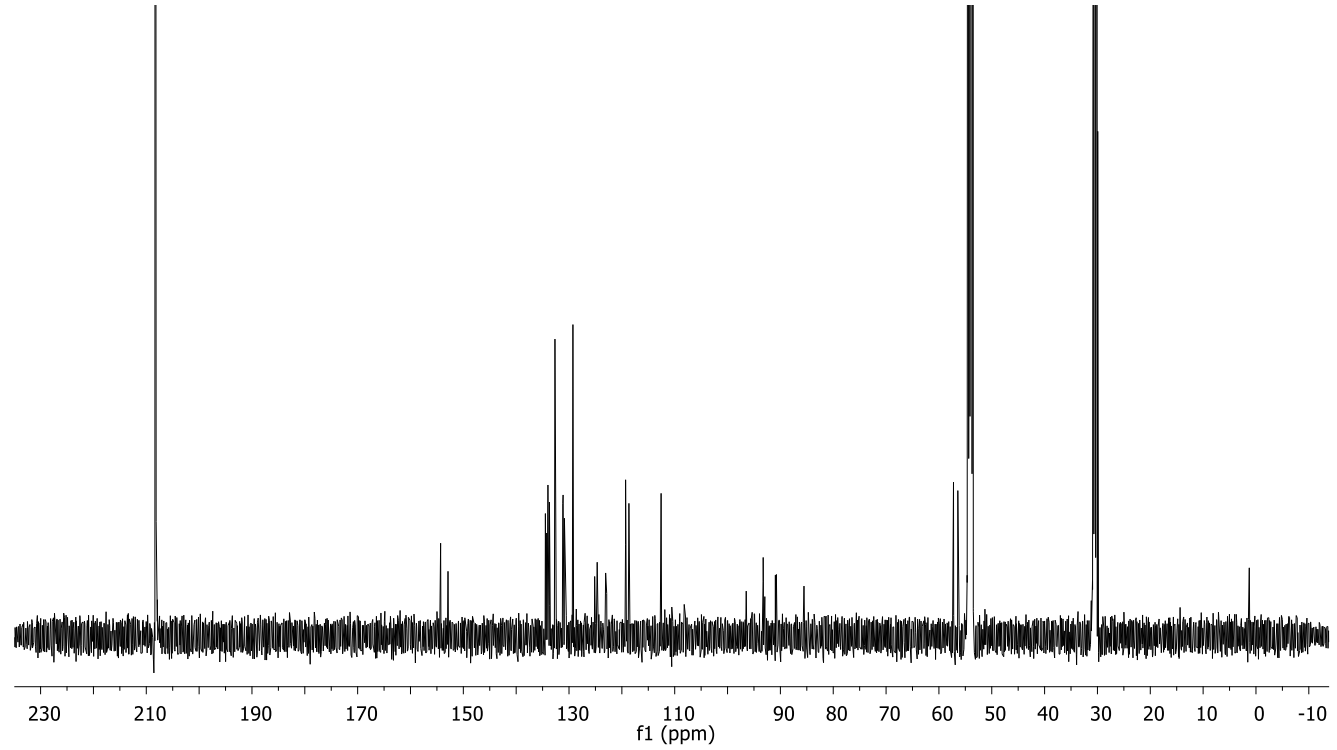



**Figure S10: 2D-NOESY analysis of the complex 15·Ag(I)**

The methoxy group located at the *ortho* position (Pink) respect to the alkyne (identify due to the cross peak A with H1 at 5.58 ppm) gave a strong NOE (crosspeak B) with the more deshielded H4 proton of the pyrene ring.

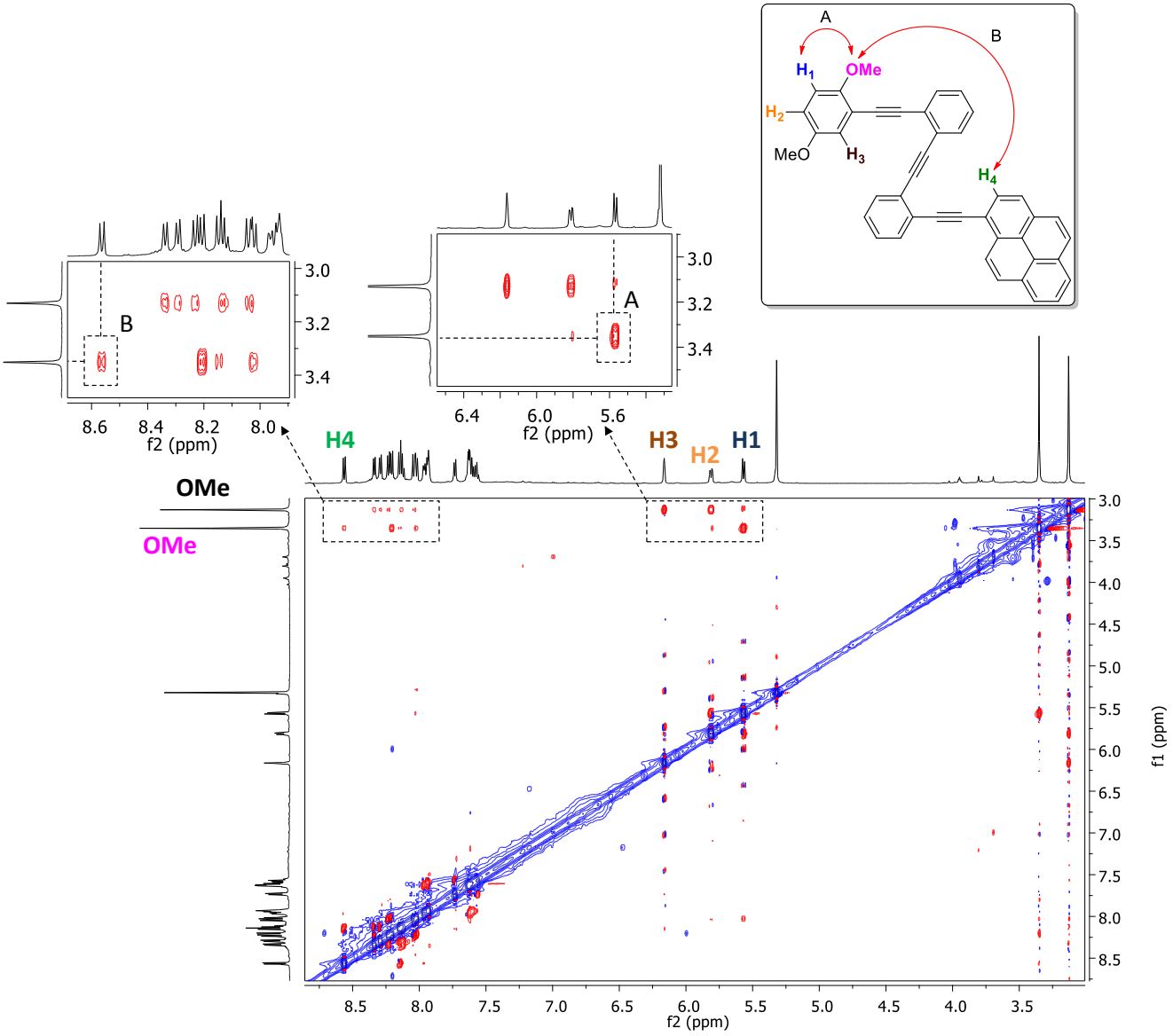


**Figure S11: 2D-NOESY analysis of the complex 17·Ag(I)**

The methoxy group located at the *ortho* position (Pink) respect to the alkyne (identify due to the cross peak A with H1 at 5.58 ppm) gave a strong NOE (crosspeak B) with the more deshielded H2 proton of the phenyl ring.